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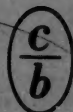
DOKLADY CHEMISTRY

**PROCEEDINGS of the
ACADEMY OF SCIENCES
of the USSR**

Chemistry Section

**ДОКЛАДЫ АКАДЕМИИ НАУК СССР
(DOKLADY AKADEMII NAUK SSSR)**

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АКАДЕМИИ НАУК СССР

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STUDY OF THE BLUE PRODUCTS OBTAINED IN THE REDUCTION OF GERMANIUM HETEROPOLY ACIDS

Acad. Sci. USSR Corresponding Member, I.P. Allmarin,
Z.F. Shakhova and R.K. Motorkina

Compounds of a blue color are usually obtained as the reduction products of various iso- and heteropoly compounds, representing the class of so-called molybdenum or tungsten "blues". The question of the composition and structure of the blue compounds is one of the most confused and least studied problems of the chemistry of heteropoly compounds.

At the present time the blues are divided into two groups, the "simple" molybdenum (or tungsten) blues, which are the derivatives of the isopolymolybdates (or isopolytungstates), and the blues that appear as the derivatives of the heteropoly acids.

The vast majority of the simple blues possess a colloidal character, they are amorphous, they fail to give distinct x-ray patterns [1], they fail to possess a strictly determined chemical composition [2], and they represent mixtures of a large number of various penta- and hexavalent molybdenum oxides [3]. The crystalline derivatives of the tungsten blues have also been studied, being the hydrogen analogs of the tungsten bronzes [4].

A large number of the simple molybdenum blues of diverse composition have been studied by Gleimser and Lutz [5], while various authors in recent years have made an x-ray photograph study of many of the crystalline molybdenum and tungsten blues [6, 7].

The molybdenum "blues" are most frequently used in analytical chemistry, being derivatives of the heteropoly acids. Usually the authors of the methods for determining the various elements as molybdenum blues indicate that it is impossible to determine the exact composition of these compounds, and they also indicate that the color intensity is dependent on the presence of foreign electrolytes, on the nature of the reducing agent, the concentration of the solutions, etc. In almost all cases only empirically developed methods are given, without any theoretical generalizations whatsoever [8]. Up to now many investigators believe that in all of the cases for the formation of the blues the same product is always obtained, namely, the simple molybdenum blue, yielding more or less stable colloidal solutions [9].

Z.M. Velsberg and B. Ya. Dain [10] were the first to clearly formulate the conclusion that the molybdenum "blues", being derivatives of hetero compounds, represent individual chemical compounds, close in structure to the original yellow forms, and not adsorption compounds. The studies made in recent years [11-13] confirm the validity of the conclusion relative to the community of structure of the reduced and unreduced forms of heteropoly compounds.

Our investigation of the absorption spectra, the electronograms and the oxidation-reduction potentials of the germanium heteropoly acids had, on the one hand, the purpose of elucidating the optimum conditions for the use of similar compounds in analysis, and on the other hand it gives the possibility of making some conclusions relative to the structure of the heteropoly blues.

We studied the absorption spectra of germanomolybdenum blue, used in analysis for the determination of germanium, and obtained by us under the conditions recommended for this determination, of germanovanadomolybdenum blue, obtained by an analogous method, and also of germanotungsten and germanovanadotungsten.

blues, which were obtained by the reduction of the corresponding heteropoly acids with divalent chromium solution (CrSO_4). In all cases the individual heteropoly acids, synthesized by the ether method, were taken for reduction, the acids, based on the analysis results, being fully saturated compounds.

The absorption spectra for all of the indicated compounds, and also for the original unreduced heteropoly acids, expressed in molar light-absorption coefficients, are shown in Fig. 1. The measurements were made in the 220-1100 m μ region, using an SF-4 spectrophotometer. It was established that all of the indicated compounds possess a very high light absorption in the ultraviolet region of the spectrum and that the absorption drops rapidly with increase in wave length.

The light absorption curves for ammonium molybdate and the germanomolybdenum and germanovanadomolybdenum heteropoly acids fail to possess any maxima in the indicated limits of wavelength variation. The replacement of two molybdenum atoms by vanadium in the germanomolybdenum heteropoly acid molecule changes the color of the compound from lemon-yellow to orange-red but fails to change the character of the light absorption curve; to be sure, the absorption is increased in the visible portion of the spectrum. The light absorption curve for the germanotungsten heteropoly acid has a distinct maximum at 265 m μ , while the germanovanadotungsten heteropoly acid has a narrow absorption band in the 260-265 m μ region.

The absorption spectra of the blues in the ultraviolet region are analogous to the absorption spectra of the original heteropoly acids, i.e. the light absorption is very great in the short wave-length portion of the spectrum and drops rapidly with increase in wave-length. For the tungsten heteropoly acids the maximum light absorption is retained at 265 m μ even after their conversion into blues, which demonstrates the community of structure of the heteropoly acid and heteropoly blue anions. All of the investigated blues differ essentially from the spectra of the original heteropoly acids in the visible portion of the spectrum by the presence of a light-absorption maximum at 825 m μ . Apparently, the presence of this second maximum on the light-absorption curve is conditioned by the creation of a blue color for the compounds as a result of increasing the polarization effects in the reduction of complexes.

The analogy in the course of the light absorption curves for the heteropoly acids and heteropoly blues is evidence that the complex anion is not decomposed in the formation of the heteropoly blues, but instead only some of the atoms in its addenda are reduced, with retention of the same arrangement that they possessed in the original heteropoly acids.

To confirm this conclusion we made an electrographic study of the sodium and ammonium molybdates and para-molybdates, of the germanomolybdenum and germanovanadomolybdenum heteropoly acids, and also of the blues, obtained in the reduction of the germanomolybdenum heteropoly acids. A vertical EM-4 electronograph, built by the State Optical Institute, was used for the work.

As a result of indexing the obtained electronograms it was established that both the germanomolybdenum and germanovanadomolybdenum heteropoly acids, and also the germanomolybdenum heteropoly blue, crystallize in the cubic syngony and possess very

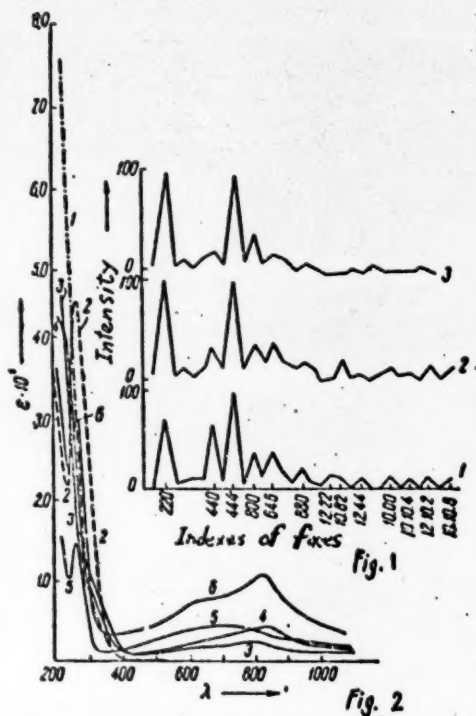


Fig. 1. Absorption spectra of germanium heteropoly acids and of their reduction products. 1 - germanomolybdenum acid, 2 - germanotungsten acid, 3 - germanomolybdenum acid, 4 - germanovanadomolybdenum acid, 5 - germanovanadotungsten acid, and 6 - germanotungsten blue.

Fig. 2. Graph comparing the experimental values of the line intensities found in the electronograms of: 1 - germanomolybdenum acid, 2 - germanovanadomolybdenum heteropoly acid, and 3 - germanomolybdenum blue.

close lattice parameters (23.05, 23.10 and 23.16 Å, respectively).

The similarity of the electronograms in the character of their diffraction patterns and in the values of the interplanar distances, and also the closeness of the elementary cell dimensions, speak for the identical type of fine structure possessed by these compounds, i.e. they speak for the same type of atomic arrangement in the molecules and for close values of the interatomic distances. From this it is evident that the formation of germanomolybdenum blue is not accompanied by decomposition of the original heteropoly acid molecule, for both the blue and the acid represent isostructural compounds. It is also evident that in the quantitative determination of various elements as heteropoly blues it is necessary, in order to obtain reproducible results, to first create conditions for the complete formation of the unreduced heteropoly acid and then subject it to reduction with the "mildest" reducing agent possible, without decomposing the heteropoly anion. In the formation of the germanovanadiomolybdenum heteropoly acid the vanadium isomorphously replaces the molybdenum in the heteropoly anion.

The graph comparing the experimental values of the line intensities found in the electronograms of the germanomolybdenum and germanovanadiomolybdenum heteropoly acids, and of germanomolybdenum blue, is shown in Fig. 2.

Since for elucidating the possibility of using the hetero blues in analysis it is necessary to know the oxidation-reduction properties of the various heteropoly compounds, it was decided to study the oxidation-reduction potentials of the germanium heteropoly acids. For their determination the method proposed by Yu.A. Chernikhov and V.G. Goryushina [14] for determining the oxidation-reduction potential of tungsten was used: the total amount of Mo^{VI} or W^{VI} in the original heteropoly compound was determined by potentiometric titration with a solution of CrSO₄, after which, to the other half of the solution, CrSO₄ was added in an amount equal to half of that consumed in the titration, and the potential of the obtained system was measured. The value of this potential corresponds to E₀.

Divalent chromium was chosen as the reducing agent, since its use makes it possible to obtain a comparative idea as to the oxidation-reduction properties of the molybdenum and tungsten heteropoly compounds. It was established that the oxidation-reduction potentials of the systems Mo^{VI}/Mo^V and W^{VI}/W^V in the heteropoly compounds are not higher, but instead are considerably lower than the potentials of the molybdenum and tungsten, not combined as complexes. Neither the molybdenum nor the tungsten, bound in the complexes (as is generally accepted), possess a high oxidation-reduction potential, but instead this high potential is all possessed by the complex heteropoly anion, which on reduction also gives a blue-colored complex anion, containing a definite amount of either molybdenum or tungsten atoms, reduced to the pentavalent state, and retaining the structure of the original complex. As a result, to study the oxidation-reduction properties of all of the heteropoly acids it is necessary, first of all, to study the oxidation-reduction properties of the system heteropoly acid/heteropoly blue, and not of the system Mo^{VI}/Mo^V or W^{VI}/W^V.

TABLE 1

	W ^{VI} /W ^V Without Complex	W ^{VI} /W ^V from Ge-W Acid	Mo ^{VI} /Mo ^V Without Complex	Mo ^{VI} /Mo ^V from Ge-Mo Acid	Ge-Mo Acid/Blue	Ge-V-Mo Acid/Re- duced Form	Ge-V-W Acid/Re- duced Form
E in rel cal	-0.396	-0.207	+0.377	+0.294	+0.455	+0.788	+0.635
E _h	+0.208	+0.040	+0.625	+0.542	+0.703	+1.036	+0.883

The oxidation-reduction potential of the system germanomolybdenum heteropoly acid/blue was determined, and also the composition of germanomolybdenum heteropoly blue by titration with K₂Cr₂O₇ and CrSO₄ solutions. It was established that the germanomolybdenum heteropoly blue contains ~1/4 of all of the molybdenum with a valence of 5, since molybdenum with lower valences can be formed only after all of the molybdenum has been reduced to the pentavalent state. The heteropoly complex exists only as long as the blue exists, and is decomposed on further reduction.

It was established that the introduction of vanadium into the heteropoly anion raises the oxidation-reduction potential of the latter considerably.

The values of the oxidation-reduction potentials for the systems studied are given in Table 1.

It is obvious that a more detailed study of the oxidation-reduction properties of the various heteropoly compounds will greatly extend the range of their use in analytical chemistry (for example, in the field of oxidation-reduction indicators).

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THE OXYGEN-CONTAINING COMPOUNDS FORMED DURING THE SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN OVER AN IRON CATALYST

A.N. Bashkirov, M.I. Khotimskaya and N.A. Orlova

(Presented by Academician A.V. Topchiev, May 27, 1955)

In recent years, extensive investigations, directed toward clarification of the mechanism and a study of the products of the synthesis, have been published in the field of catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen utilizing assorted catalysts and process conditions.

Synthesis of hydrocarbons from carbon monoxide and hydrogen is always accompanied by the formation of oxygen-containing compounds, the percentage of which depends on the nature of the catalysts and the process conditions. Iron catalysts cause the formation of more oxygen-containing compounds than do cobalt catalysts [1,2].

In the literature, there is described a process for the synthesis of hydrocarbons over an iron catalyst, in which process about 18% of the converted carbon monoxide goes to oxygen-containing compounds which are equally divided between the water and hydrocarbon phases [3]. A detailed study of the composition of the compounds formed in the synthesis process is of interest both from the point of view of the possibility of preparing valuable chemical products and from the point of view of clarifying the mechanism of the synthesis, the latter with the aim of improving and further developing the process.

We have previously described the isolation and investigation of the water-soluble oxygen-containing compounds contained in the aqueous condensate and formed during a synthesis over an iron catalyst [4].

The water-soluble oxygen-containing compounds for the most part comprise C_1 to C_4 alcohols (predominately ethyl alcohol), but the water layer also contains acids (acetic, propionic, and butyric), acetaldehyde, propionaldehyde, acetone, and methyl ethyl ketone.

The aim of the present work was the isolation and identification of the oxygen-containing compounds contained in the hydrocarbon phase of the product (fraction boiling up to 200°) formed during the synthesis of hydrocarbons from carbon monoxide and hydrogen over an iron catalyst at a moderate pressure and at a 1:1 ratio of carbon monoxide to hydrogen in the feed gas. The hydrocarbon fraction investigated had d_4^{20} 0.7370, an acid number of 6.5, a hydroxyl number of 36.0, a carbonyl number of 13.1, and a saponification number of 2.7 mg KOH per gram.

Compounds containing a carboxyl group were isolated by treating the product investigated with a 20% soda solution. A 3650-gram portion of the synthesis product was taken for the investigation. The amount of acids comprised about 1% (37.2 g). The isolated acids were distilled into narrow fractions having temperature ranges corresponding to the boiling points of the individual acids, and the acids were characterized by physical constants and by the silver content of the silver salts prepared from them. Moreover, the amides were prepared from the fractions boiling at $160-164^\circ$ and $184-187^\circ$, and when these amides were mixed, respectively, with *n*-butyramide and *n*-valeramide, no melting point depression was obtained.

The data, presented in Table 1, on the properties of the isolated fractions are in complete agreement with those for individual normal acids of the paraffin series.

TABLE 1

Properties of the Isolated Acids

Fraction No.	Boiling point (°C)	d_4^{20}	n_D^{20}	Acid, No. mg KOH/g	Ag in silver salt %		Melting point of amide (°C)	Acid identified
					Found	Calculated		
3	138—142	0.9900	1.3880	758	59.70	59.64	—	Propionic
7	160—163	0.9605	1.3981	641	55.47	55.35	115—115.2	n-Butyric
9	184—188	0.9394	1.4060	556	51.80	51.64	105—105.5	n-Valeric
9	200—205	0.9278	1.4178	495	48.60	48.40	—	n-Caproic
11	221—225	0.9161	1.4270	437	45.69	45.54	—	n-Enanthic

TABLE 2

Properties of the Isolated Aldehydes

Fraction, No.	B. p. (°C)	n _D ²⁰	Aldehyde number, mg KOH/g	Dimedone derivatives						Aldehyde identified
				M. p. (°C)	Found %		Calculated %		Empiri- cal for- mula	
					C	H	C	H		
2	47--50	1.3640	959.0	154—154.5	71.23	8.82	71.25	8.75	C ₁₉ H ₃₈ O ₄	Propionaldehyde
4	72—75	1.3847	770.0	133—134	71.87	8.98	71.85	8.98	C ₂₀ H ₃₈ O ₄	n-Butyraldehyde
6	100—103	1.3945	640.5	104.2—104.7	72.45	9.24	72.41	9.19	C ₂₁ H ₃₈ O ₄	n-Valeraldehyde
8	125—128	1.4108	553.0	108.3—108.9	72.98	9.42	72.92	9.40	C ₂₂ H ₃₈ O ₄	n-Caproaldehyde
10	150—153	1.4250	483.2	102—102.7	73.46	9.55	73.40	9.58	C ₂₃ H ₃₈ O ₄	n-Enanthic aldehyde
12	166—170	1.4276	430.4	89—90	73.96	9.77	73.85	9.74	C ₂₄ H ₃₈ O ₄	n-Caprylic aldehyde

TABLE 3

Properties of the Isolated Alcohols

Fraction No.	B. p. (°C)	d_4^{20}	n_D^{20}	Hydroxyl No. mg KOH/g	Phenylurethans				Alcohol identified
					M. p. (°C)	Empirical formula	N, %		
							Found	Calculated	
3	115—117	0.8092	1.3938	756.0	59—59.5	$C_{11}H_{21}O_2N$	7.20	7.25	n-Butyl
6	135—138	0.8149	1.4106	634.0	45.7—45.9	$C_{13}H_{23}O_2N$	6.71	6.76	n-Amyl
8	155—159	0.8195	1.4187	558.0	40.4—41.0	$C_{15}H_{27}O_2N$	6.38	6.33	n-Hexyl
10	72—75/10 mm	0.8230	1.4256	485.0	58—59	$C_{17}H_{31}O_2N$	5.92	5.95	n-Heptyl
13	85—88/10 mm	0.8266	1.4310	434.6	73.2—74	$C_{19}H_{35}O_2N$	5.58	5.62	n-Octyl
15	97—100/10 mm	0.8283	1.4331	382.1	61—61.9	$C_{21}H_{39}O_2N$	5.27	5.31	n-Nonyl
17	112—115/10 mm	0.8305	1.4375	350.2	60—60.7	$C_{23}H_{43}O_2N$	5.01	5.05	n-Decyl

The neutral oxygen-containing compounds were isolated from the investigated product by chromatographic adsorption on 60-100 mesh ASM brand silica gel having an activity of 17.1. The separation was carried out in a standard, water cooled column 1.5 meters high, Pentane served as the wash liquid, while ethyl ether was used as the eluant. From 3500 grams of product there was obtained 289 grams of dark yellow oxygen-containing com-

TABLE 4

Properties of the Isolated Ketones

Fraction No.	B. p. (°C)	n_D^{20}	Carbonyl number mg KOH/g	2,4-Dinitrophenylhydrazones				Ketone identified
				M. p. (°C)	Empirical formula	N, %		
						Found	Calculated	
2	77—80	1.3820	784.0	110—110.8	$C_{10}H_{18}O_4N_4$	22.05	22.21	Methyl ethyl ketone
4	100—103	1.3901	661.5	142—143	$C_{11}H_{18}O_4N_4$	21.09	21.21	Methyl n-propyl ketone
6	125—128	1.4058	570.5	105.2—106	$C_{12}H_{18}O_4N_4$	20.30	20.14	Methyl n-butyl ketone
8	150—152	1.4129	507.2	88—88.7	$C_{13}H_{18}O_4N_4$	19.35	19.18	Methyl n-amyl ketone
10	170—174	1.4170	448.0	57—58	$C_{14}H_{20}O_4N_4$	18.47	18.30	Methyl n-hexyl ketone
12	192—195	1.4188	409.3	87—88	$C_{15}H_{22}O_4N_4$	17.31	17.50	Methyl n-heptyl ketone

pounds ("concentrate") characterized by the following data: d_4^{20} 0.8300, n_D^{20} 1.4275, hydroxyl number, 147.5; carbonyl number, 102.7 (aldehyde number, 49.2); saponification number, 23.5 (in mg KOH/gram).

The following method was used for the resolution of concentrate. Isolation of the aldehydes was accomplished by treating the concentrate with freshly prepared sodium bisulfite solution and subsequently decomposing the bisulfite-addition compound. 43 grams of a mixture of aldehydes was obtained. The latter was distilled into fractions which were characterized by their dinedone derivatives (Table 2).

The alcohols from the concentrate, separated from the aldehydes, were isolated as the boric acid esters with subsequent saponification of the borates. In all, 128 grams of a mixture of alcohols was isolated and fractionated in a column having 30 theoretical plates. The physical constants of the narrow fractions were determined, and the phenylurethans were prepared (Table 3).

The ketones in the product were isolated by treating the product with a mixture of equal quantities of semicarbazide hydrochloride and sodium acetate. Upon decomposition of the semicarbazones which separated from the remainder of the concentrate, 54 grams of ketones were isolated, and these were distilled in the column. The separated fractions were characterized by the preparation of derivatives of 2,4-dinitrophenylhydrazine (Table 4).

Thus, from the product (boiling up to 200°) of the synthesis of hydrocarbons from CO and H_2 at moderate pressure over an iron catalyst there was obtained, by chromatographic adsorption, a concentrate comprising neutral oxygen-containing compounds.

From the concentrate were isolated and identified: aldehydes—propionaldehyde, n-butyraldehyde, n-valeraldehyde, n-enanthic aldehyde, and n-caprylic aldehyde; ketones—methyl ethyl, methyl propyl, methyl butyl, methyl amyl, methyl hexyl, and methyl heptyl ketone; alcohols—n-butyl, n-amyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, and n-decyl alcohol. The total alcohol content of the investigated product was 3.7%, and the total carbonyl compound content was 2.8%. About 1% of a mixture of acids was isolated from the product investigated, these acids consisting of propionic, n-butyric, n-valeric, n-caproic, and n-enanthic acid.

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STUDY OF THE REACTIONS OF ALCOHOLS AND KETONES WITH PENTABORANE

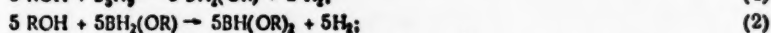
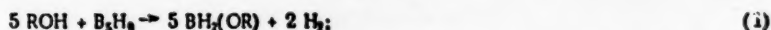
A.F. Zhigach, E.B. Kazakova and R.A. Kigel

(Presented by Academician A.N. Nesmeyanov, July 11, 1955)

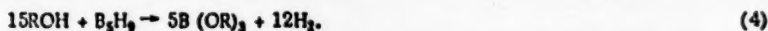
There is nothing in the literature on the reactions of alcohols and ketones with pentaborane. Only some very limited literature data are presented on the reaction of alcohols and ketones with other boron hydrides; with diborane [1,2] and with tetraborane [3,4].

In the present work the reactions of methyl, ethyl and butyl alcohols and of acetone with pentaborane are described.

It was experimentally established that the alcohols react with pentaborane to form intermediate compounds — the alkoxyborines. The action of small amounts of the absolute alcohols on pentaborane leads to partial hydrogen evolution, and further addition of the alcohol leads to additional hydrogen evolution. The hydrogen evolution process is completely ended only after 15 moles of alcohol per mole of pentaborane have been added. The final reaction result is the formation of the boric acid ester and the evolution of 12 moles of hydrogen. The reaction course can be depicted by the following equations:



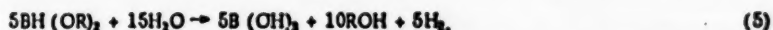
the complete equation is:



When the alcohol is added to the pentaborane in amounts corresponding to the stoichiometric proportions given in Equation (4) the reaction proceeds quantitatively in the direction of forming the boric acid ester, both at room temperature and under cooling to -20° , and with much heat evolution. By reacting the corresponding alcohols with pentaborane we were able to synthesize the methyl, ethyl and butyl esters of boric acid. The obtained esters were isolated and analyzed.

The presence of reactions (1) and (2) was established by hydrolyzing the reaction product — the dialkoxyborine, which, in accord with these equations, was obtained from stoichiometric amounts of ethyl alcohol and pentaborane.

The hydrolysis of this product proceeds rapidly at 0° with the evolution of 5 moles of hydrogen, in accordance with the equation:



Practically no hydrolysis at 0° was observed in the presence of Reaction (4), since here the formed boric acid ester and the unreacted pentaborane (due to insufficient alcohol) are hydrolyzed very slowly at this temperature.

The diethoxyborine was also isolated in pure form when the reaction was run with stoichiometric amounts of ethyl alcohol and pentaborane, in accord with Equations (1) and (2), and was analyzed.

The presence of reaction (5) leads to the situation that the alcohol, diluted with water, reacts very rapidly with pentaborane, with the quantitative evolution of hydrogen and the formation of boric acid. These reactions

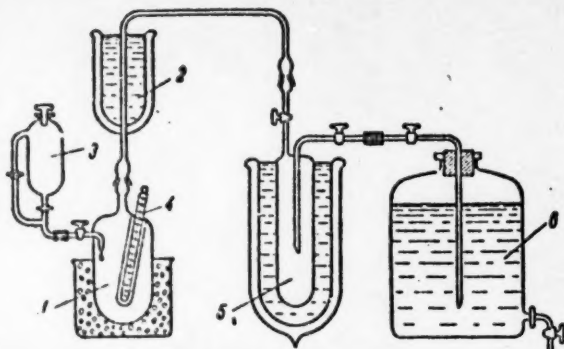


Fig. 1.

can serve for the quantitative analysis of alcohols and of pentaborane.

The reaction between pentaborane and acetone is exothermic, both at room temperature and at -80° , with the formation of a clear colorless solution. The reaction course is complex. Distillation of the reaction mixture gave three liquid fractions and a solid still residue. The fraction with b.p. $139-140^\circ$ was obtained in 25-30% yield, and from its analysis is isopropyl borate. Hydrogen fails to be evolved when dry acetone is reacted with pentaborane. Aqueous acetone solutions react very violently with pentaborane. The reaction proceeds with the evolution of much heat and gas. An excess of aqueous acetone leads to complete decomposition of the pentaborane to boric acid. This reaction can serve as a convenient method for the quantitative determination of boron in pentaborane.

EXPERIMENTAL

All of the experiments were run with pentaborane that had been carefully freed of impurities by distillation through a rectification column fitted with a total reflux head. The distilled pentaborane had the following constants: b.p. $60.0-60.2^\circ$ at 760 mm; m.p. -46.5° ; d_4^{20} 0.625.

Found %: B 85.6; H 14.3

B_2H_6 . Calculated %: B 85.64; H 14.36

The alcohols were first treated with fused calcium oxide and then were distilled from metallic sodium. The acetone was dried over calcium chloride and then distilled. All of the reactions with pentaborane were run in a hydrogen atmosphere.

Reaction of Ethyl Alcohol with Pentaborane. The reaction was run in a special apparatus (see Fig. 1), consisting of reaction vessel 1, fitted with a reflux condenser 2, a type of Dewar vessel with liquid ammonia, dropping funnel 3 and thermometer 4, vessel 5 for trapping the vapors, and gasometer 6 for measuring the gas.

To 1.7 g (0.0269 mole) of pentaborane, cooled with ice water, was added from the dropping funnel 18.5 g (0.403 mole) of ethyl alcohol at such a rate that the temperature in the vessel failed to rise above 10° . To accelerate the reaction after adding the alcohol the reaction mixture was heated on the boiling water bath until the evolution of hydrogen ceased. The amount of liquid obtained was 19.2 g, which corresponds to a 95% yield of the ethyl borate. The product distilled completely from a Claisen flask at a temperature of $117.5-118.0^\circ$ at 745 mm. According to the literature [6], ethyl borate has b.p. $118.3-118.4^\circ$ at 740.5 mm.

* It was experimentally established by us that the boiling point of pentaborane is $60 \pm 0.2^\circ$ at 760 mm instead of 58.1° , the latter given in the literature [5] on the basis of vapor pressure calculations.

Found %: C 48.9; 49.6; H 10.15; 10.3; B 7.43; 7.36
B (OC₂H₅)₃. Calculated %: C 49.30 H 10.36; B 7.41

The Reaction of Methyl Alcohol with Pentaborane was run under analogous conditions. For reaction there was taken 1.3 g (0.0206 mole) of pentaborane and 9.9 g (0.309 mole) of methyl alcohol. There was obtained 10.3 g of methyl borate, or a yield of 92%. The obtained product distilled completely at 68-69.5°; d_4^{20} 0.928; n_D^{20} 1.352. Literature [7]: b.p. 67.7-67.8°; d_4^{20} 0.932; n_D^{24} 1.3558.

Found %: C 34.3; 33.9; H 8.6; 8.9; B 10.4; 10.61
B (OCH₃)₃. Calculated %: C 34.66; H 8.73; B 10.41

The Reaction of n-Butyl Alcohol with Pentaborane was run under analogous conditions. For reaction there was taken 0.95 g (0.0151 mole) of pentaborane and 16.7 g (0.226 mole) of n-butyl alcohol. The yield of butyl borate was 15 g, or 85%. The reaction products distilled completely at 236-239° at 750 mm, d_{27}^{27} 0.8553. Literature: b.p. 234-238° [8] at 745 mm; d_{27}^{27} 0.856.

Found %: C 62.8; 62.0; H 11.6; 11.45; B 4.65; 4.60
B (OC₄H₉)₃. Calculated %: C 62.6; H 11.83 B 4.7

Reaction of Acetone with Pentaborane. The reaction was run in the same apparatus and under the same conditions as before. To 1.6 g (0.0256 mole) of pentaborane was added 22 g (0.38 mole) of acetone.

The obtained reaction mixture was distilled: Fraction I to 58°, 5.3 g; Fraction II 58-139°, 4.5 g; Fraction III 139-140°, 5.4 g; solid still residue, 7.0 g.

Analysis of Fraction III

Found %: C 57.34; 57.50; H 11.45; 11.33; B 5.48; 5.65
B(i-OC₃H₇)₃. Calculated %: C 57.5; H 11.26; B 5.72

According to the literature isopropyl borate has b.p. 140° [9].

Diethoxyborine was prepared in the same apparatus. To 0.7 g (0.011 mole) of pentaborane was added 5.0 g (0.11 mole) of absolute ethyl alcohol at -20°. The obtained solution was kept at room temperature for 10 minutes, after which it was vacuum-distilled at 0° under fractional condensation: the vapors were passed through the receivers at temperatures of -30 and -78°. There was obtained 2.3 g of solution at -78°, which corresponds to a diethoxyborine yield of 40%. The product was hydrolyzed with an excess of water and the amounts of evolved hydrogen and formed boric acid were determined quantitatively.

Found %: B 10.77; 10.48; H 1.01; 0.97
BH (OC₂H₅)₂. Calculated %: B 10.62; H 0.98

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THE RELATIONSHIP BETWEEN STRUCTURE, COLOR AND SUBSTANTIVITY OF DYES - BENZANILIDE DERIVATIVES

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(Presented by Academician B.A. Kazansky, July 15, 1955)

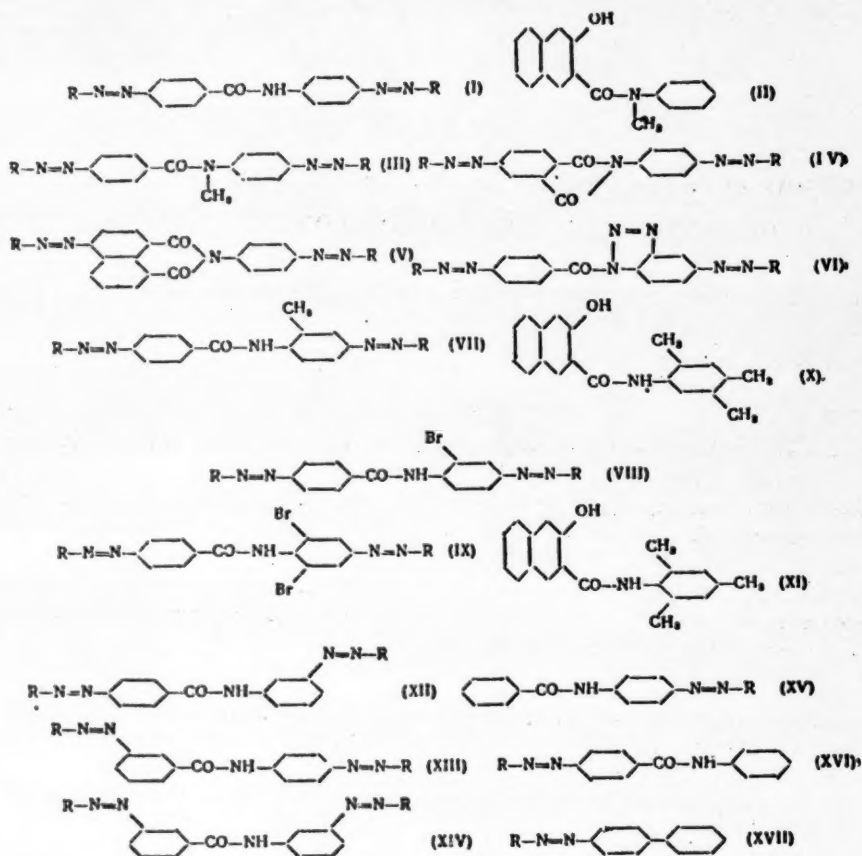
The derivatives of benzanilide have attracted much attention lately as dyes, many of them possessing great affinity for cellulose fibers. The dyes from 4,4'-diaminobenzanilide (I)*, proposed as direct dyes, are in no way inferior to the benzidine dyes in substantivity. The bisdiaz compound, formed in the diazotization of 4,4'-diaminobenzanilide, the same as the bisdiazotized benzidine, possesses a valuable property: the diazo groups enter into the azo-coupling reaction at different speeds, and this makes it possible to introduce the diazo compound into the azo-coupling reaction with two different azo-components and, consequently, to obtain dyes of different colors and hues. The purpose of the present work was to study the relationship existing between the structure of the dyes derived from benzanilide and their color and substantivity.

On the basis of much experimental material, accumulated by various investigators in studying the relationships existing between dye structure and substantivity, at the present time it can be considered as established that the most important criteria of the direct dyes are: 1) the presence in the dye molecules of a long chain of conjugated double bonds; 2) the possibility for planar distribution of the dye molecules on the fiber; 3) the presence in the dye molecule of groups that can form hydrogen bonds with the cellulose. These rules were established for the most part by the method of studying the benzidine dyes. In our approach to a study of the derivatives of benzanilide as dyes we placed these rules at the base, taking into consideration here the fact that a considerable difference exists in the structure of the two classes of dyes - the derivatives of biphenyl and the derivatives of benzanilide.

We will not dwell here on the synthesis portion of this work; some of the dyes investigated by us have been described, and some were prepared by us for the first time. In all cases the azo-coupling was run in alkaline medium. The obtained dyes were purified by chromatographing on aluminum oxide; for the removal of mineral impurities they were precipitated from aqueous solutions with sodium acetate and the acetate impurity was removed by heating the precipitate with alcohol.

We used the following method to determine the substantivity. The weighed sample of dye, calculated on the basis of 0.00002 mole of dye for 1 g of the fabric (calico) to be dyed, was dissolved in water with the addition of 2% of soda and 20% of common salt, based on the weight of the fabric. The bath ratio was kept constant (1:30) in all of the experiments. The dyeings were made at 80° for 1 hour. Under these conditions it is possible to achieve close to the maximum rate of dye pickup by the fabric. The control solutions, prepared in exactly the same manner as the dye solutions, were kept at the same temperature and for the same length of time as the latter in the dye bath. After dyeing, the solutions were cooled to room temperature, the fabric squeezed, and then always washed with the same amount of cold distilled water until the wash waters were practically colorless, which were then added to the rest of the solution. The control and dye solutions were made up to the same volumes and analyzed colorimetrically on the electrophotocolorimeter. We took as the substantivity value the amount of dye in percent, removed from the dye bath during the dyeing operation, minus the amount of dye that was removed by the cold distilled water in washing the dyed calico until the wash waters were practically colorless.

*R is the azo-component.



First of all the question of the importance of the amide hydrogen atom on the development of dye substantivity was studied. Krzikalla and Eistert [1] showed that substitution of the amide hydrogen atom in the azotol molecule leads to a sharp decrease in substantivity. Thus, for example, the *N*-methyl derivative of azotol A (II) shows very slight substantivity. The above mentioned investigators explained this phenomenon as being due to the impossibility of the substituted azotols forming the enol structure. A paper [2] was published recently on the potentiometric titration of solutions of azotol alkaline salts; on the basis of the obtained experimental data the author of this paper comes to the conclusion that it is possible for the azotols to exist in the enol form.

TABLE 1

Dye	Azo-Component					
	ASG acid			Chicago SS acid		
	Substan- tivity %	λ max m μ		Substan- tivity %	λ max m μ	
		water	cello- phane		water	cello- phane
I	63	550	575	56	550	570
III	3	530	540	2	525	530

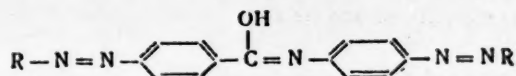
TABLE 2

Dye*	Substan- tivity %	λ max m μ	
		water	cello- phane
I	63	550	575
VII	51	540	570
VIII	55	535	560
IX	30	525	535

*R is the azo-component of ASG acid.

We synthesized and studied the *N*-methyl derivatives of the dyes that were prepared from 4,4'-diaminobenzanilide (III). These dyes proved to be practically devoid of substantivity (see Table 1).

We had already communicated earlier [3] on the sharp reduction in substantivity that takes place when either a five- or six-membered cycle or the triazole ring (IV, V, VI) is closed. Apparently, the high substantivity possessed by the dyes obtained from 4,4'-diaminobenzanilide, the same as for the azotols, despite the difference in the structure of these compounds, can be explained as being due to the possibility of forming the enol structure. The following interrelationship exists between color and substantivity: in most cases the appearance of substantivity is accompanied by deepening of the color, which, in all probability, is associated with the fact that both of these dye properties depend in considerable measure on the chain length of the conjugated double bonds [4]. The enol form of the dyes obtained from 4,4'-diaminobenzanilide contains a long chain of conjugated double bonds between the auxochromes:



V.A. Izmailsky and E.A. Smirnov, who made a detailed study of the color of various benzanilide derivatives, do not exclude the possibility of these compounds existing in the enol form [5]. That tautomerism is possible for many amides is also indicated in the studies of other investigators, in which number [6-8] are included.

TABLE 3

Dye	Azo-Component			
	ASG acid		Chicago SS acid	
	Substan- tivity %	λ_{max} m μ	Substan- tivity %	λ_{max} m μ
I	63	550	58	550
XII	24	525	50	530
XIII	27	530	23	530
XIV	13	520	9	520

TABLE 4

Dye	Substan- tivity %
XV	23
XVI	23
XVII	5

As a result, it can be considered very probable for the dyes derived from benzanilide and, in particular, the dyes obtained from 4,4'-diaminobenzanilide, to exist in two tautomeric forms. It is quite possible that in the fixation on the fiber the equilibrium is shifted toward the more deeply colored and more substantive enol form, which form is preferentially absorbed by the fiber. In support of this is the considerable increase in depth of shade that is shown by the dyes prepared from 4,4'-diamino-

benzanilide when used to dye cellophane; at the same time the dyes obtained from the *N*-methyl derivative of 4,4'-diaminobenzanilide show considerably higher color in water solution and deepen the shade on cellophane but slightly (see Table 1)*.

Attention is drawn to the fact that the weakening of interaction between the two parts of the dye molecule as the result of steric difficulties, removing the molecule from the coplanar state, and reducing the conjugation effect, and in this way making difficult the formation of the enol structure, leads to heightened color and reduced substantivity. Dye (IX), containing two bromine atoms in the ortho-position to the nitrogen of the amide group, deepens its shade on cellophane considerably less than do the dyes in which these positions are either not substituted (I) or only one substituent is introduced (VII, VIII) (Table 2).

A similar influence of steric difficulties on the substantivity of the azotols was observed by Splegler [9], who made a comparison of the affinities of the azotols (X) and (XI) toward cellulose fibers, whereas the first of these azotols shows considerable substantivity, the second is practically devoid of substantivity.

It was of interest to compare the dyes from 4,4'-diaminobenzanilide with the corresponding bisazo dyes, for which either one or both of the azo groups are found in the meta-position to the amide group. This com-

*It should be mentioned that the shades on cellophane, independent of the structure of the dyes, have absorption maxima that are shifted by 5-10 m μ toward the long-wave region of the spectrum when compared with the absorption maxima for the water solutions of the same dyes. Thus, the dye, aniline \rightarrow ASG acid, in solution has its maximum absorption at 520 m μ , while its very light shade on cellophane shows maximum absorption at 530 m μ .

parison revealed that the dyes from the 3,4'-, 4,3'- and 3,3'-diaminobenzanilides (XII, XIII, XIV) show less substantivity and are more highly colored than their isomeric dyes from 4,4'-diaminobenzanilide (Table 3).

Apparently, the reason for the heightened color and reduced substantivity of these dyes is to be sought in the absence in their molecules of a chain of conjugated double bonds between the auxochromes: even in the presence of the enol structure, there fails to be such a chain for the dyes (XII-XIV). It is also possible that the structure of these dyes is less favorable for the formation of hydrogen bonds between the dye auxochromes and the cellulose. In addition, it can be assumed that tautomeric rearrangement proceeds with greater difficulty for these dyes than it does for the dyes from 4,4'-diaminobenzanilide. In this connection the work of N.A. Valyashko and M.V. Boltina should be mentioned, who established the presence of the imino alcohol structure for diacetyl-para-phenylenediamine, but who failed to show a similar structure in neutral solution for the corresponding meta- derivative [6].

Apparently, the reaction between the dyes derived from benzanilide and cellulose leads to the formation of hydrogen bonds, not only between the cellulose and the auxochromes, but also between the cellulose and the amide group of the dye. This is indicated from a comparison of the substantivity of the dyes prepared from the 4- and 4'-aminobenzanilides (XV, XVI) with the dye prepared from 4-aminodiphenyl (XVII), in the molecule of which the amide group is absent: the azo-component in all three dyes is ASG acid (Table 4).

The dyes (XV) and (XVI) are hardly inferior in substantivity and are close in shade to the bisazo dyes, in which one of the azo groups is found in the meta-position to the -CO-NH- group; they show a greater affinity toward the cellulose fiber than does the dye (XIV) with two azo groups in the meta-position to the amide group.

A comparison of the data, given in Tables 3 and 4, indicates that the number of azo groups and their arrangement in the benzene rings of the benzanilide residue shows a great influence on substantivity of dyes; the dyes derived from 4,4'-diaminobenzanilide differ sharply in both substantivity and depth of shade from all of their other isomeric bisazo dyes derived from benzanilide*.

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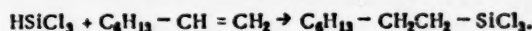
*T.V. Oleinik participated in the experimental portion of this work.

ADDITION OF METHYLDICHLOROSILANE AND ETHYLDICHLOROSILANE TO ALLYL HALIDES

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Corresponding Member A.D. Petrov

Sommer, Pietrusza and Whitmore [1], having successfully added HSiCl_3 to 1-octene in the presence of diacetyl peroxide, showed the possibility in principle of applying the Kharasch reaction to the synthesis of silane hydrides.



Later it was found that other compounds also enter into this reaction: HSiBr_3 [2,3], $\text{CH}_3\text{SiHCl}_2$ [3-5], $\text{C}_2\text{H}_5\text{SiHCl}_2$ [3,5], $\text{C}_6\text{H}_5\text{SiHCl}_2$ [3,5], $(\text{C}_2\text{H}_5)_2\text{SiHCl}_2$ [3,5], $(\text{C}_6\text{H}_5)_2\text{SiHCl}$ [3,5], $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{SiHCl}$ [3,5], SiH_4 [6,7], $\text{Cl}_3\text{SiCH}_2\text{SiHCl}_2$ [8], $(\text{C}_6\text{H}_5)_3\text{SiH}$ [9], and even various olefins [1-8, 10, 11], dienes [3, 5, 12, 13], acetylene hydrocarbons [4, 14, 15], alkenyl chlorides [11, 12, 15], unsaturated acids [9], alkenylsilane chlorides [4, 15-17], and vinyl and allyl ethers [21].

An increase in the complexity of the silane hydride structure, also of the original olefin, either in the presence of peroxides or under ultraviolet illumination, leads, as a rule, to considerable reduction in the yield of the addition product [4, 11], while such silane hydrides as triethoxysilane and triethylsilane could not be made to add to 1-octene at all [11].

In addition to peroxides and ultraviolet light, the addition can also be run in the presence of AlCl_3 , AlBr_3 or ZnCl_2 [18] or simply at 200-400° under pressure [3,5].

Before we pass over to a discussion of the present work, it is necessary to mention the following:

1. Burkhard and Krieble were unable to add HSiCl_3 to styrene [4] in the presence of diacetyl peroxide due to the side reaction of styrene polymerization.
2. The addition of HSiCl_3 to allyl chloride [14] and to trichloroethylene [15] proceeds with difficulty in the presence of peroxides, and in low yields.
3. Platinized carbon, in the presence of which the side polymerization reactions are suppressed, gives ex-

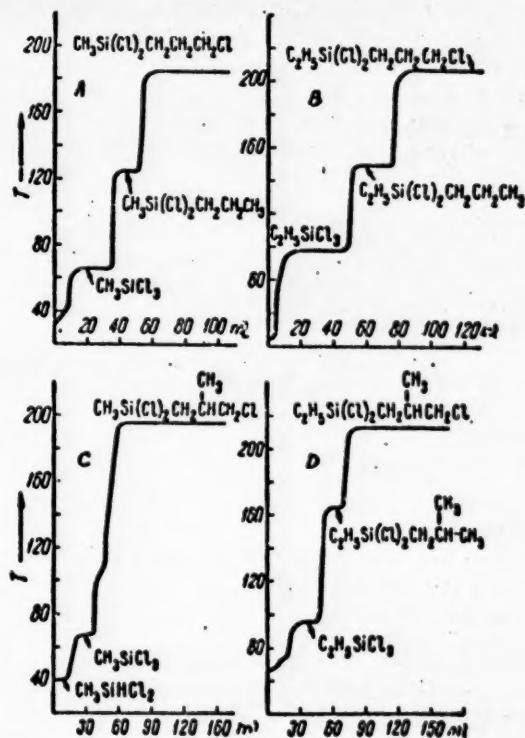


Fig. 1.

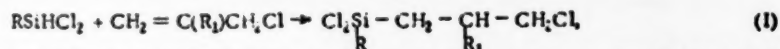
cellent yields in these cases (HSiCl_3 with styrene or butadiene), as was shown by Wagner and coworkers [19], and somewhat later by Bailey and Pines [12].

HSiCl_3 also adds to allyl chloride, in the presence of platinized carbon, as has been communicated by Bailey and Pines, who, however, failed to give any experimental data relative to the reaction conditions and, especially, the yield of addition product.

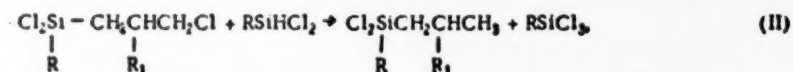
Continuing our study of the addition reactions of olefins to silane hydrides [20], and also with the purpose in mind of synthesizing from available silane hydride compounds containing functional groups in the γ -position to silicon, we studied the possibility of adding, in the presence of platinized carbon, the silane hydrides that are more complex than silicochloroform (HSiCl_3), such as methylchlorosilane ($\text{CH}_3\text{SiHCl}_2$) and ethylchlorosilane ($\text{C}_2\text{H}_5\text{SiHCl}_2$), to allyl halides (allyl chloride, methallyl chloride, etc.). In view of the fact that replacement of the chlorine in HSiCl_3 by alkyl groups, in the case of using either peroxides or ultraviolet light, is accompanied by considerable reduction in the yield of addition products, we had very little hopes of success at first. However, actually it was found that both the methylchlorosilane and the ethylchlorosilane, in the presence of platinized carbon containing 1% of platinum, easily add at 160° , and in excellent yield, to allyl chloride and to methallyl chloride, forming the corresponding γ -chloroalkylalkyldichlorosilanes. Together with this, as can be seen from the distillation curves, shown in Fig. 1, the following side products are also formed together with the γ -chloroalkylalkyldichlorosilanes: CH_3SiCl_2 , $\text{C}_2\text{H}_5\text{SiCl}_2$, $\text{CH}_3\text{Si}(\text{Cl})_2\text{C}_2\text{H}_5$, $\text{CH}_3\text{Si}(\text{Cl})_2(\text{i-C}_4\text{H}_9)$ and $\text{C}_2\text{H}_5\text{Si}(\text{Cl})_2(\text{i-C}_4\text{H}_9)$.

In the case of methallyl chloride these side products are formed in considerably smaller amount. If $\text{CH}_3\text{SiHCl}_2$ and $\text{C}_2\text{H}_5\text{SiHCl}_2$ are compared in this respect, then it can be seen that the methylchlorosilane is less subject than the ethylchlorosilane to these side reactions. Thus, if in the reaction of $\text{CH}_3\text{SiHCl}_2$ with methallyl chloride, the formation of $\text{CH}_3\text{Si}(\text{Cl})_2(\text{i-C}_4\text{H}_9)$ can be judged only on the basis of a slight inflection on the distillation curve (see Fig. 1 B), then in the case of $\text{C}_2\text{H}_5\text{SiHCl}_2$ the corresponding ethylisobutyldichlorosilane was isolated in appreciable amount. Approximately the same conclusion can be made if Figs. 1 A and 1 B are compared. Disproportionation products are mainly formed in the reactions of $\text{CH}_3\text{SiHCl}_2$ and $\text{C}_2\text{H}_5\text{SiHCl}_2$ with allyl bromide, the chief of which are CH_3SiCl_3 and $\text{C}_2\text{H}_5\text{SiCl}_3$.

As a result, the above permits making the postulation that if the main reaction is expressed by the equation:



where $\text{R} = \text{CH}_3$, C_2H_5 ; $\text{R}_1 = \text{H}$, CH_3 , then apparently, the secondary reaction can be expressed by the equation:



although in the last case it is possible for the secondary products to be formed by other methods, the elucidation of which does not enter into the problem of the present study.

γ -Chloropropylmethylchlorosilane. A mixture of 76 g of allyl chloride, 115 g of methylchlorosilane and 0.5 g of platinized carbon was charged into an autoclave, the pressure in which was then raised to 10 atm. by means of nitrogen. The mixture was heated at 160° for 6 hours. After cooling, the pressure in the autoclave was 12 atm. The reaction products were distilled through a 35-theoretical plate column (Fig. 1 A). There was obtained:

1. 25 ml CH_3SiCl_2 ; b.p. 65° (750 mm).
2. 13.5 g $\text{CH}_3\text{Si}(\text{Cl})_2\text{C}_2\text{H}_5$; b.p. 124.4° (750 mm); n_D^{20} 1.4250; d_4^{20} 1.0383; found MR = 38.69, calculated MR = 38.80.

Found %: H 6.79; 6.67; C 31.85; 31.79; Cl 44.19; 44.45; Si 17.54; 17.30.
 $\text{C}_4\text{H}_{10}\text{SiCl}_2$. Calculated %: H 6.42; C 30.58; Cl 43.14; Si 17.86.

Literature [3]: b.p. $123-124^\circ$ (747 mm).

3. 60 g (30% of the theoretical) $\text{CH}_3\text{Si}(\text{Cl})_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$; b.p. 184.5° (754 mm); n_D^{20} 1.4580; d_4^{20} 1.2045; found MR = 43.39, calculated MR = 43.64.

Found %: H 5.03; 4.98; C 25.78; 25.52; Cl 55.24; 55.66; Si 14.33; 14.20.
 $C_4H_7SiCl_3$. Calculated %: H 4.74; C 25.08; Cl 55.53; Si 14.65.

γ -Chloropropylethylchlorosilane. From 76 g of allyl chloride and 130 g of ethyldichlorosilane under the same conditions (0.5 g of platinized carbon, initial pressure 10 atm., 160°, 6 hrs.), distillation of the reaction products (Fig. 1 B) gave:

1. 36 ml $C_2H_5SiCl_3$, b.p. 98° (745 mm).
2. 26 g $C_2H_5Si(Cl)_2C_3H_7$, b.p. 150° (745) n_D^{20} 1.4370; d_4^{20} 1.0343; found MR = 43.35, calculated MR = 43.43.

Found %: C 34.81; 34.95; H 7.14; 7.15; Si 16.32; 15.83; Cl 41.30; 41.45.

$C_5H_{12}SiCl_2$. Calculated %: C 35.09; H 7.07; Si 16.40; Cl 41.44.

3. 60 g (29% of the theoretical) $C_2H_5Si(Cl)_2CH_2CH_2CH_2Cl$; b.p. 206° (743 mm); n_D^{20} 1.4661; d_4^{20} 1.1809; found MR = 48.22; calculated MR = 48.27.

Found %: H 5.33; 5.25; C 29.30; 29.36; Cl 51.43; 51.62; Si 14.30; 14.29.

$C_5H_{11}SiCl_3$. Calculated %: H 5.39; C 29.21; Cl 51.74; Si 13.66.

(γ -Chloro- β -methylpropyl)methyldichlorosilane. From 90 g of methallyl chloride and 115 g of methyldichlorosilane under the same conditions there was obtained (Fig. 1 C):

1. 15 ml CH_3SiCl_3 , b.p. 66° (747 mm).
2. 120 g (58% of the theoretical) $CH_3Si(Cl)_2CH_2CH(CH_3)CH_2Cl$; b.p. 195.5° (745 mm); n_D^{20} 1.4629; d_4^{20} 1.1703;

found MR = 48.37, calculated MR = 48.27.

Found %: H 5.22; 5.39; C 29.40; 29.54; Cl 49.86; 49.80; Si 14.00; 13.86.

$C_5H_{11}SiCl_3$. Calculated %: H 5.39; C 29.21; Cl 51.74; Si 13.66.

(γ -Chloro- β -methylpropyl)ethyldichlorosilane. From 90 g of methallyl chloride and 130 g of ethyldichlorosilane under the same conditions there was obtained (Fig. 1 D):

1. 20 ml $C_2H_5SiCl_3$, b.p. 96-97° (743 mm).
2. 18 g $C_2H_5Si(Cl)_2CH_2CH(CH_3)CH_2Cl$, b.p. 165° (743 mm), n_D^{20} 1.4400, d_4^{20} 1.0179; found MR = 47.94; calculated

MR = 48.06.

Found %: H 7.54; 7.64; C 38.94; 39.20; Si 14.33; 14.73.

$C_6H_{14}SiCl_2$. Calculated %: H 7.62; C 38.92; Si 15.16.

3. 106 g (48% of the theoretical) $C_2H_5Si(Cl)_2CH_2CH(CH_3)CH_2Cl$; b.p. 213° (746 mm); n_D^{20} 1.4676; d_4^{20} 1.1525;

found MR = 52.93, calculated MR = 52.90.

Found %: H 5.96; 6.03; C 33.10; 32.94; Cl 48.31; 48.19; Si 12.66; 12.93.

$C_6H_{13}SiCl_3$. Calculated %: H 5.97; C 32.81; Cl 48.44; Si 12.78.

γ -Chloropropylmethyldiethylsilane. To the Grignard reagent, prepared from 21 g of Mg in 350 ml of ether and 96 g of C_2H_5Br , was added 80 g of $CH_3Si(Cl)_2CH_2CH_2CH_2Cl$. The mixture was heated for 4 hours, after which the ether was removed by distillation and the residue was fractionally distilled in vacuo to give 22 g (30% theoretical) $(C_2H_5)_2Si(CH_3)CH_2CH_2CH_2Cl$; b.p. 58-59.5° (3 mm); n_D^{20} 1.4498, d_4^{20} 0.9011; found MR = 53.29, calculated MR = 53.64. In another experiment where the distillation through a column was made at atmospheric pressure the $(C_2H_5)_2Si(CH_3)CH_2CH_2CH_2Cl$ decomposed with the evolution of gaseous products and the formation of a considerable amount of $(CH_3)(C_2H_5)_2SiCl$; b.p. 118.6° (746 mm); n_D^{20} 1.4206; d_4^{20} 0.8853; found MR = 39.10, calculated MR = 39.17.

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THE VIBRATIONAL SPECTRA OF OLEFINS

CALCULATION AND INTERPRETATION OF THE VIBRATIONAL SPECTRA OF PROPYLENE AND DEUTEROPROPYLENE

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The propylene molecule is the simplest representative of the alkyl-substituted ethylenes. It appeared of interest to make a calculation and interpretation of the vibrational spectra for this molecule, since such data might be of help in elucidating the characteristic properties of the vibrational spectra for the homologous $\text{RCH}=\text{CH}_2$ series.

In the best case the propylene molecule can have only one plane of symmetry (the C_s point group). There are 21 normal vibrations: 14 of the vibrations are symmetrical (A') and 7 are antisymmetrical (A'') with respect to the plane of symmetry. All of them are active, both in the Raman and in the infrared spectra.

The vibrational spectra of propylene have been studied by many investigators. Fox and Martin [1] studied the infrared spectra of propylene solutions in CCl_4 in the $2800\text{--}3600\text{ cm}^{-1}$ region. Wilson and Wells [2] studied the infrared spectra of propylene vapors in the $400\text{--}1700\text{ cm}^{-1}$ region. Avery and Ellis [1] obtained the infrared spectra of propylene (both as vapors and in the solid state) in the $800\text{--}1700\text{ cm}^{-1}$ region. Rasmussen and Bratain [3] studied the infrared spectra of propylene vapors in the $2\text{--}15\mu$ region. The infrared spectra of propylene vapors and of propylene- d_6 , using an apparatus of high resolving power, were obtained by Lord [4] in the $400\text{--}6200\text{ cm}^{-1}$ region. The Raman spectra of propylene were studied by the authors of the papers [5]. The frequency assignments of propylene have been examined in the studies of many authors [2-4,6], however, up to now there has not been a generally accepted interpretation of the vibrational spectra for propylene (see Table 1).

We will now discuss the frequency assignments to be found for the deformational vibration of the $\text{C}=\text{C}$ in propylene- d_6 . Lord [4] assigns a frequency of $\sim 410\text{ cm}^{-1}$ to this vibration. The author failed to observe any absorption in this region. The magnitude of this frequency was determined from an interpretation of the frequency 539 cm^{-1} as being composed of $410 + 130$, in which connection the value of 130 cm^{-1} for the rotational vibration frequency of the CD_3 group around the $\text{C}=\text{C}$ bond was also determined from this interpretation. Such an assignment does not seem convincing to us, since the frequencies for propylene- d_6 ($1154, 1174, 691\text{ cm}^{-1}$), which the author interprets as being composed with participation of the 130 cm^{-1} frequency, can also be easily interpreted by another method. Calculation shows that the deformational vibration frequency for $\text{C}=\text{C}=\text{C}$ $\text{CD}_3\text{CD}_3 = \text{CD}_3$ has a value of $\sim 340\text{ cm}^{-1}$, i.e. in the transition from propylene to propylene- d_6 , the $\text{C}=\text{C}=\text{C}$ frequency is reduced by $\sim 90\text{ cm}^{-1}$. This conclusion is supported when a comparison with the spectra of acetaldehyde and $\text{CD}_3-\text{C}(\text{D})=\text{O}$ is made: in the transition from $\text{CH}_3-\text{C}(\text{H})=\text{O}$ to $\text{CD}_3-\text{C}(\text{D})=\text{O}$ the deformational vibration frequency for $\text{C}=\text{C}=\text{O}$ is shifted from 515 to 422 cm^{-1} , i.e. also by approximately 90 cm^{-1} .

A calculation of the vibrational spectra for propylene was made by a number of authors. Wilson [2] calculated the frequency values in the region below 2000 cm^{-1} with the aid of the force coefficients obtained from other molecules. However, it is impossible to acknowledge this calculation as being satisfactory, since, first,

TABLE 1

Interpretation of the Vibrational Spectra for Propylene and Propylene- d_3

Coordinates	Symmetry	CH ₃ CH = CH ₂						CD ₃ CD = CD ₂					
		Sverdlov		Raman	Herzberg [6]	Pitzer [7]	Rasmussen [3]	Lord [4]	Sverdlov	Infrared	Calcd.	Observed	
		Calcd.	Infrared		Observed	Observed	Observed	Observed					
$\text{q}_{\text{CH}_2}^-(\text{C}-\text{H})$	A'	3099	3090 (a)	3087 (c)	3081	~3050		3090	2326	2331 (a)		2331	
$\text{q}_{\text{CH}_2}^+(\text{C}-\text{H})$	A'	3011	2992 (a)	2990 (f)	2979	~3050		2992	2225	2224 (a)		2219	
$\text{a}_{\text{H}}^-(\text{HCH})$	A'	1431	1419 (b)	1415 (g)	1416	1415		1298	1111			1012	
$\text{b}^-(\text{C} = \text{CH}_2)$	A'	1150	1172 (c)		1224	1172	731	1229	959			872	
$\text{Q}_b^-(\text{C}=\text{C})$	A'	1651	1652 (d)	1648 (h)	1647	1649		1652	1575	1588 (d)		1588	
$\text{Q}_b^+(\text{C}-\text{C})$	A'	3016	3013 (a)	3010 (i)	3012	~3050		3013	2252	2240 (a)		2240	
$\text{B}_2^-(\text{HC}=\text{C})$	A''	1293	1298 (a)	1297 (h)	1297	1297	1297	1419	1025	1022 (b)		1033	
$\text{Y}_{ab}(\text{C}-\text{C}=\text{C})$	A'	441	428 (c)	432 (g)	417	417	417	428	340			(410)**	
$\text{Q}_3^-(\text{C}-\text{C})$	A'	887	920 (b)	920	919	920	920	920	59	788 (c)		788	
pCH_2	A''	915	912 (d)		1166	911	913	912	712	712 (d)		712	
xCH_2	A''	982	991 (a)		578	990	578	578	741	734 (a)		434	
pCCH	A''	558	578 (d)	580 (j)	936	580	990	991	433	434 (a)		734	
$\text{b}^-(\text{HCC})$	A'	951	963 (e)		1043	1042	1170	1172	709	691		868	
$\text{b}^-(\text{HCC})$	A''	1040	1045 (b)		996	1050	1044	1045	845	872 (b)		788	
$\text{q}_{\text{H}_3}^-(\text{C}-\text{H})$	A'	2976	2954 (d)	2956 (e)	2916	~2950		2933	2224	2204 (a)		2204	
$\text{q}_{\text{CH}_3}^+(\text{C}-\text{H})$	A'	2899	2933 (a)	2924 (h)	2852	~2950		2870	2103	2130 (b)		2130	
$\text{q}_{\text{CH}_3}^-(\text{C}-\text{H})$	A''	2975	2954 (d)	2956 (e)	2960	~2950		2954	2221	2219 (d)		2224	
$\text{a}^+(\text{HCH})$	A'	1381	1378 (b)		1399	~1370		1378	1101			1022	
$\text{a}^-(\text{HCH})$	A'	1469	1474 (a)		1448	1444		1474	1075	1061		1061	
$\text{a}^-(\text{HCH})$	A''	1472	1443 (d)	1448 (c)	1472	1444		1443	1070	1049 (d)		1049	

*Rasmussen [3] gave an interpretation for the frequencies below 1300 cm^{-1} .**The 410 cm^{-1} line was not observed.

Note: (a) strong; (b) medium; (c) weak; (d) very strong; (e) very weak; (f) weak, polarized; (g) medium, polarized; (h) very strong, polarized; (i) strong, polarized; (j) weak, depolarized.

the system of force coefficients for ethane and ethylene, used by the author, was erroneous, and, second, the author neglected to take many of the reaction constants into consideration. Thus, it is natural for the difference between the calculated and observed frequencies to be as high as $\sim 110 \text{ cm}^{-1}$ and many of the frequencies were assigned incorrect values*. Pitzer and Kilpatrick [7] calculated the antisymmetrical vibrational frequencies for propylene, in which connection the authors failed to discount the C-H and HCH vibrations in their calculation, and also neglected a number of important reaction constants. Consequently, their calculation also appears to be slightly gross.

We calculated the normal vibrations for propylene by the method of M.A. Elyashevich [8]. As natural vibrational coordinates we will choose the variation in the lengths of the bonds and in the values of the angles $q_i, \beta_i (i = 1, 2, 3), q_j, \beta_j (j = 1, 2, 3), Q_a, Q_b, a_{12}, \gamma_{ab}, \beta_{23}, d'_{jk}$ (see Fig. 1) $\rho_{CH_2}, \rho_{CCH}, \chi_{CH_2}^{CCH}$. Here ρ_{CH_2} and ρ_{CCH} are angles, determining the emergence of the C=C bond from the plane of the CH_2 and CCH groups; $\chi_{CH_2}^{CCH}$ is the angle of rotation of the groups CH_2 and CCH with respect to each other. There are three supplementary conditions between the natural coordinates. The geometric parameters adopted in [10] were used for the calculation. The force coefficients needed for the calculation were taken from the calculations for ethylene [9], ethane, propane [8] and isobutylene [10]. Some of the constants were determined by the method of varying the constants: $K_{CH} (C-H) = 8.4; K_{C_2} = 0.7; u_{\rho_{CCH\beta_1}} = -0.028$ (in 10^6 cm^{-2} units).

The 14th and 6th degree roots of the secular equations were calculated by the method of successive drawing of diagonals [8]. In Table 1 are given the calculated and observed frequencies and also an interpretation of the vibrational spectra. The agreement between the calculated and observed frequencies is good: the maximum error equals 33 cm^{-1} , while the average error is 13 cm^{-1} . By using the assignments of the fundamental frequencies it is possible to interpret all of the remaining observed values as being either combinations or overtones (see Table 2).

TABLE 2

Interpretation of the Combination Frequencies and Overtones

$CH_2CH = CH_2$		$CD_2CD = CD_2$	
Infrared	Assignment	Infrared	Assignment
570 (a)	991-428	539 (b)	1588-1049
601 (a)	1652-1045	868 (c)	434 + 434
615 (b)	1045-428	1012 (b)	2130-1111
987 (e)	1419-428	1033 (c)	691 + 340
1143 (e)	578 + 578	1154 (b)	1588-434
1190 (e)	1045 + 578-428	1174 (c)	2224-1049
1229 (c)	1652-428	2042 (e)	1022 + 1022
1466 (b)	1045 + 428	2065 (c)	1049 + 1022
1825 (a)	912 + 912	2080 (b)	1061 + 1022
1977 (c)	991 + 991	2719 (e)	1588 + 1111
2034 (c)	1045 + 991	3319 (e)	2219 + 1111
2090 (e)	1045 + 1045	3341 (e)	2331 + 1022
2222 (e)	1298 + 920	4402 (c)	2204 + 2204
2461 (e)	1298 + 1172		
2736 (b)	1443 + 1298		
2870 (b)	1443 + 1443		

From the calculations it follows that the frequencies 3087; 2990; 1415; 1172; 1648; 3010; 1297; 432; 912; 991 cm^{-1} are characteristic for the coordinates, corresponding to the group $H_2CH = CH_2$. Since this group enters into all of the molecules of type $RCH = CH_2$, then from this it follows that these frequencies should also be characteristic for the homologous $RCH = CH_2$ series. This conclusion is well supported by the Raman spectra data for the n-alkenes** (see Table 3). The characteristic nature of many of the indicated frequencies was noted earlier

*The results obtained by the authors are given in the monograph [8].

**The frequency of 2990 cm^{-1} for the symmetrical valence vibration of the C-H group in CH_4 is so weak that it fails to be observed.

by a number of authors when they analyzed their experimental data: P.A. Bazhulin and Kh.E. Sterin [11] indicated the characteristic nature of the frequencies: 3087; 3000; 1642; 1416, and 1297 cm^{-1} , while Goubeau [12] mentions the characteristic nature of all of the above indicated group of frequencies (with the exception of 1166 cm^{-1}). However, nothing is said in these studies as to which type of vibrations many of these frequencies belong

In conclusion I consider it my pleasant duty to thank Academician G.S. Landsberg for looking over this work and for his valuable comments.

TABLE 3

Characteristic Frequencies of the n-Alkenes $\text{RCH}=\text{CH}_2$

Molecules	Coordinates									
	$\bar{\nu}_{\text{CH}_2} (\text{C-H})$	$\nu_2 (\text{C-H})$	$\nu (\text{C=C})$	$\nu_{12} (\text{CH}_2)$	$\nu' (\text{C=CH}_2)$	$\nu_2 (\text{HC=CH})$	$\nu (\text{C=C=O})$	ν_{CH_2}	$\nu_{\text{CH}} \times \text{CH}_2$	ν_{CH}
C_2H_4	3087	3010	1648	1415	1172	1207	432	912	991	580
C_3H_6	3084	2998	1642	1416	1166	1194	437	908	980	623
C_4H_8	3083	3001	1642	1416	1169	1202	435	909	991	627
C_5H_{10}	3082	3003	1642	1418	1155**	1190	433**	913	996	634
C_6H_{12}	3081	3000	1642	1417	1163	1204	437	911	997	627
C_7H_{14}	3080	3001	1642	1417	1167	1203	437	911	993	631
C_8H_{16}	3079	2999	1642	1416	1157	1197	442	910	987	633
C_9H_{18}	3078	2996	1642	1413	1157	1196	445	910	987	634
$\text{C}_{10}\text{H}_{20}$	3081	3001	1642	1417	1166**	1192	437	911	993	634
$\text{C}_{11}\text{H}_{22}$	3080	2996	1642	1415	1158	1199	436	907	997	631
$\text{C}_{12}\text{H}_{24}$	3084	3008	1643	1415	1174	1199	437	912	992	636
$\text{C}_{13}\text{H}_{26}$	3078	2999	1642	1416	1161	1200	429	908	992	632
$\text{C}_{14}\text{H}_{28}$	3077	2997	1640	1413	1181	1207		908		635

*Data of Bazhulin and Sterin [11].

**Data of Goubeau [12].

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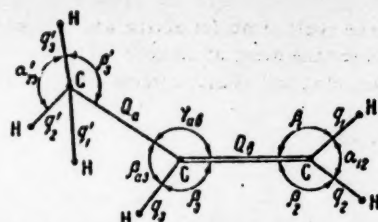


Fig. 1.

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STUDY OF THE TRANSFORMATIONS OF SODIUM PHOSPHOTUNGSTATE UNDER THE INFLUENCE OF SODIUM HYDROXIDE

Acad. Sci. USSR Correspondent Member Vict. I. Spitsyn and E.A. Fabrikova

Beginning with 1940, E.A. Nikitina [1] published a number of papers on the subject of preparing the multisubstituted salts of certain heteropoly acids, in which number the sodium phosphotungstates are included, by the method of adding the calculated amount of alkali to a solution of less substituted salt. The results obtained in this manner agreed with the theory proposed by Miolati [2] and by Rosenheim [3] for the structure of heteropoly compounds, in accord with which the formula $H_2[P(W_2O_7)_6 \cdot xH_2O]$ is assigned to phosphotungstic acid. Basing himself on the x-ray structure analysis data [4], B.V. Nekrasov [5] emerged with a criticism for holding such an opinion with respect to the nature of the compounds obtained in this manner and postulated that the "highly substituted" phosphomolybdates are binary salts — the reaction products of the unsaturated heteropoly compound and the acid molybdate, formed as the result of the hydrolysis of the original saturated compound.

To obtain an answer to this confused problem we decided to study the reaction of sodium hydroxide with the usually obtained trisubstituted sodium phosphotungstate, the composition of which is given in Table 1 (Preparation No. 1). To a 25% aqueous solution of this salt we added the calculated amount of sodium hydroxide in such a manner that there was 1 mole of NaOH for 1 mole of the phosphotungstate. To check on the chemical homogeneity of the reaction product we used the method of sequential crystallization. On evaporating the solution, satisfying the conditions for the preparation of the tetrasubstituted salt, in a vacuum-desiccator over P_2O_5 , it was found that the composition of the first fraction of crystals corresponds to the trisubstituted salt (Table 1, Preparation No. 2); while in the second fraction of crystals, already isolated with difficulty from the viscous filtrate, the atomic ratio of Na:P is close to that required for the tetrasubstituted salt (Table 1, Prepara-

TABLE 1

Analysis of the Obtained Products

Preparation Nos.	Amount in %				Formulas of Oxides
	Na ₂ O	P ₂ O ₅	WO ₃	H ₂ O	
1	2.90	2.29	86.53	8.28	2.97Na ₂ O·P ₂ O ₅ ·23.6WO ₃ ·29.2H ₂ O
	2.99	2.23	86.30	8.48	
2	3.08	2.28	85.29	9.35	3.11·Na ₂ O·P ₂ O ₅ ·23.2WO ₃ ·33.4H ₂ O
	3.04	2.23	85.10	9.63	
3	3.66	2.15	81.80	12.39	4.06Na ₂ O·P ₂ O ₅ ·24.0WO ₃ ·47.3H ₂ O
	3.74	2.02	81.65	12.59	
4*	4.96	2.39	92.65	—	4.72Na ₂ O·P ₂ O ₅ ·23.4WO ₃ ·xH ₂ O
	5.07	2.45	92.48	—	
5	8.07	2.05	79.18	10.70	9.07Na ₂ O·P ₂ O ₅ ·23.4WO ₃ ·41.5H ₂ O
	8.15	2.09	78.87	10.89	
6	3.97	2.88	83.31	9.84	3.16Na ₂ O·P ₂ O ₅ ·17.6WO ₃ ·26.7H ₂ O
	4.04	2.91	83.31	9.74	
7	8.12	2.02	79.28	10.58	9.12Na ₂ O·P ₂ O ₅ ·23.8WO ₃ ·40.6H ₂ O
	8.18	2.07	79.39	10.36	
8	1.70	2.36	88.20	7.74	1.67Na ₂ O·P ₂ O ₅ ·23.2WO ₃ ·26.2H ₂ O
	1.73	2.31	88.19	7.77	
9	1.86	2.19	87.73	8.22	1.88Na ₂ O·P ₂ O ₅ ·23.9WO ₃ ·28.6H ₂ O
	1.85	2.32	87.70	8.13	

*Analysis based on anhydrous compound.

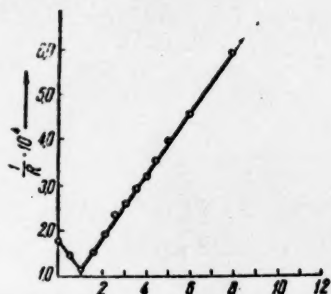
tion No. 3). Further crystallization proved unsuccessful since the mother liquor on evaporation congealed into a glassy mass with crystalline inclusions. This product (Table 1, Preparation No. 4) contained a relatively greater amount of sodium than did the second fraction of crystals. The crystalline portion of the indicated mixture is soluble in acetone and, judging from its composition and chemical properties, is the trisubstituted sodium phosphotungstate. The glassy portion fails to dissolve in acetone, but instead is only partially dehydrated by it, being converted into a white friable product that is readily soluble in water. Evaporation of the aqueous solution again gives a glassy mass. A similar separation into the soluble trisubstituted salt and an insoluble residue was also observed when the second fraction of crystals, having a composition close to that of the tetrasubstituted salt, was treated with acetone.

The acetone-insoluble product, according to the analysis data, has the composition $9.07 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 23.4\text{WO}_3 \cdot 41.5\text{H}_2\text{O}$ (Table 1, Preparation No. 5). A study of its properties revealed that it is also insoluble in alcohol and ether; the pH of aqueous solutions of the product depends on the concentration and ranges from 3.8 to 4.8. When an aqueous solution of the described compound is treated with a large excess of AgNO_3 there occurs partial precipitation of both the tungstate and the phosphorus, with retention of their atomic ratio of 1:12. Exactly the same result is obtained under BaCl_2 treatment. However, the addition of either KCl or NH_4Cl to a solution of the studied salt fails to produce any precipitates.

On the basis of these data it is impossible to consider the product obtained by us as being either the nonasubstituted derivative of the saturated acid, the K , Rb and NH_4 salts of which are difficultly soluble, or as a mixture of unsaturated luteo compounds with tungstates, since luteo compounds are soluble in acetone, alcohol and ether. There remained the not excluded variation of forming either a binary or complex salt from the unsaturated compound and the normal tungstate, arising in the hydrolysis of the original saturated heteropoly compound. The indicated postulation was verified experimentally by the method of synthesizing the desired compound directly from the unsaturated phosphotungstate and the normal sodium tungstate. The sodium phospho-9-tungstate was obtained by boiling an aqueous solution containing the calculated amounts of H_3PO_4 and Na_2WO_4 . Recrystallization from acetone gave the salt as six-sided yellow plates. Its composition based on the analysis data was $3.16 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 17.6\text{WO}_3 \cdot 26.7\text{H}_2\text{O}$ (Table 1, Preparation No. 6).

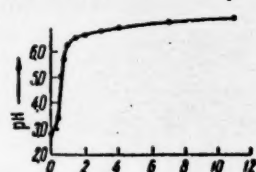
On the curve for the conductometric titration of this salt with Na_2WO_4 solution there is found a well-defined minimum at a molar ratio of phospho-9-tungstate to Na_2WO_4 equal to 1:1 (see Fig. 1). Under these conditions there is a jump in the pH value from 3.4 to 6.2, which jump is also to be found on the curve for the potentiometric titration of the indicated solutions (see Fig. 2).

By evaporation *in vacuo* over P_2O_5 and by treating the obtained residue with acetone, it was established that the solution characterized by minimum electrical conductivity contains the acetone-soluble sodium phospho-9-tungstate and our already known acetone-insoluble product of composition $9.12 \text{ Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 23.8\text{WO}_3 \cdot 40.6\text{H}_2\text{O}$ (Table 1, Preparation No. 7) in the atomic ratio of 9:1 for the $\text{Na}:\text{P}$. The similarity of Preparations Nos. 7 and 5 (Table 1) is obvious not only from their external appearance and complete chemical identity, but also from the appearance of their x-ray patterns (Fig. 3).



Moles of Na_2WO_4 per mole of phospho-9-tungstate

Fig. 1. Curve for the conductometric titration of a solution of sodium phospho-9-tungstate with Na_2WO_4 solution.



Moles of Na_2WO_4 per mole of phospho-9-tungstate

Fig. 2. Curve for the potentiometric titration of a solution of sodium phospho-9-tungstate with Na_2WO_4 solution.

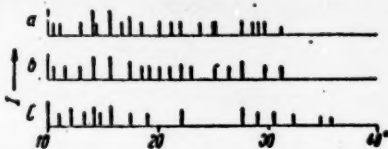
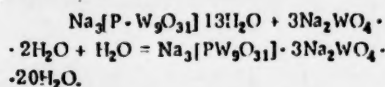


Fig. 3. Angles of reflection under x-ray photography with the aid of a Cu anode, a and b - Preparation No. 5, c - Preparation No. 7 (Table 1). I - relative intensity of the lines.

The mixing of the sodium phospho-9-tungstate with solutions of acid tungstates (meta- or paratungstate) fails to lead to the formation of new chemical compounds. Treatment of the mixture, evaporated to dryness, with acetone permits the complete separation of the phospho-9-tungstate from the meta- and paratungstates.

The reaction between the luteo salt and the normal sodium tungstate can be described by the equation:



The deviation of the minimum on the conductometric titration curve from the point, corresponding to the complete transition of the luteo compound into the binary salt, should, apparently, be explained by the need of a definite pH for the medium in order for this process to take place. The transformations, proceeding at higher pH values, are already accompanied by decomposition of the complex ions into simpler ions.

To verify such a postulation we synthesized a number of stable sodium phosphotungstate preparations, close in composition to the disubstituted salt, and labeled at the phosphorus with P^{32} (Table 1, Preparations Nos. 8 and 9). From the two salts obtained in this manner were prepared several 50-ml solutions, each solution containing the same amount of the phosphotungstate (0.0002 mole) and a variable amount of added caustic (from 0.0002 to 0.0050 mole). To reach equilibrium the solutions were kept for a day, after which the pH values of the solutions were determined.

That the sodium phosphotungstate is decomposed, accompanied by the cleavage of phosphate and the normal tungstate, was established by two methods (see Table 2). When working with the first method the reaction product is precipitated by treatment with quinoline acetate. Here the free phosphate remained in solution. The use of the labeled phosphotungstate made it possible to follow the progress of the decomposition by the rise in activity in the filtrate, or by its decrease in the precipitate. The second method was based on the fact, established by us, that there is no isotopic exchange of phosphorus between sodium phosphotungstate and sodium phosphate. The labeled phosphate Na_2HPO_4 with a known specific activity, was added to the alkaline solutions of the stable sodium phosphotungstate. The mixing of the labeled phosphate-ions with the phosphate ions, formed in the decomposition of the heteropoly compound, leads to the situation that the reverse process to the formation of heteropoly anions, evoked by the addition of hydrochloric acid and heat, already proceeds with seizure of the labeled phosphorus. The degree of decomposition taking place here is calculated from the decrease in the specific activity of the added phosphate after separating the salts in acid solution by the method of potassium phosphotungstate precipitation. The fact that comparative results are obtained in the two methods indicates that the decomposition of the sodium phosphotungstate into sodium phosphate and tungstate begins at $\text{pH} > 6$ after 5 moles of NaOH have been added for 1 mole of the disubstituted salt. The heteropoly anion suffers complete decomposition after the addition of approximately 25 moles of alkali for 1 mole of the phosphotungstate. A comparison of the shown alkali consumption with the amount of tungsten, bound with the phosphorus prior to NaOH addition, shows that the decomposition of the heteropoly compound is accompanied by the formation of the normal tungstate.

On comparing all of the obtained data the final conclusion can be made that in the addition of small amounts of sodium hydroxide to a sodium phosphotungstate solution there occurs partial decomposition of the saturated salt with the formation of the phospho-9-tungstate and the normal sodium tungstate. These last two compounds, reacting with each other, give a new chemical compound of the type of a binary or complex salt. The reactions taking place here correspond to the equation:

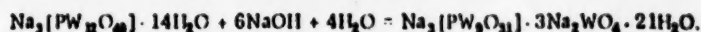


TABLE 2

Decomposition of Sodium Phosphotungstate Into Sodium Phosphate and Tungstate

Amount of NaOH added in Moles per Mole of Salt	Atomic ratio of Na:P in the solution	pH of the solution	Amount of Phosphorus Cleaved as Phosphate (%)	
			Method 1	Method 2
0	2:1	2.4	0	0
1	3:1	2.9	0	0
2	4:1	3.6	0	0
4	6:1	5.0	0	0
5	7:1	6.2	6.0	0
7	9:1	7.2	24.0	20.0
10	12:1	7.5	39.1	35.0
20	22:1	8.2	68.2	70.5
25	27:1	9.0	95.1	98.6

Not excluded is the possibility that the described binary salt is an intermediate product in the synthesis of the saturated salt from the sodium phosphate and tungstate.

The authors wish to thank Yu.P. Simanov for taking and deciphering the x-ray photographs related to this work.

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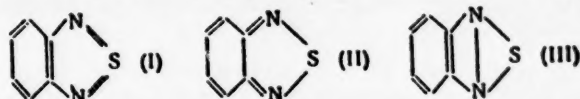
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THE CHEMISTRY OF PIAZOTHIOLE (3,4-BENZO-1,2,5-THIODIAZOLE)

A. M. Khaletsky, V. G. Pesin and Chzhao Chzhi-Chzhun

(Presented by Academician I. N. Nazarov, September 26, 1955)

The structure of piazothiole can be depicted by several formulas, for example:



The synthesis of piazothiole [1] and some of its chemical properties point to structure (I); while, for example, a measurement of the interatomic distances, made by Luzzati [2], permits assuming structure (II) — the same as for benzofurazan.

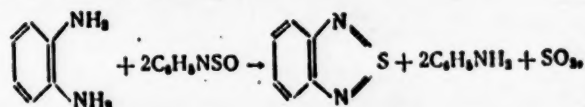
L. S. Efros and R. M. Levit [3], on the basis of studying the absorption spectra and other data, come to the conclusion that piazothiole has a quinoid structure, i.e. it has structure (II). The experimental data being developed in our studies in the field of piazothiole chemistry still do not permit making any final conclusions as to its structure.

Our earlier established fact is confirmed in the present communication, namely, that in principle there is no difference in the reactions of 1,2-phenylenediamine and 4-nitro-1,2-phenylenediamine with thionyl chloride; in both cases, under identical conditions, piazothiole and 4-nitropiazothiole are respectively formed in yields of 85-90%.

The most distinct similarity in the reactivity of the two *o*-diamines appears when the reaction with thionyl chloride is run in the presence of tertiary bases (pyridine, triethylamine). In this case both of the reactions proceed with the same vigor and in yields of 90% and higher. The reaction also proceeds successfully with other *o*-phenylenediamine derivatives, substituted in the 4 position.

However, for certain *o*-phenylenediamine derivatives the latter reaction, apparently, is not applicable, as for example, for the *o*-diamines of type: $C_6H_3(NH_2)_2X$, where $X = -OH, -COOH, -SO_3H, -SH, -S-S-R, -S-S-Ar, -NH_2$, etc.

The studied derivatives of this type can easily be synthesized by the method developed by us for the reaction of *o*-phenylenediamine with thionylaniline:



which in a number of cases proceeds with exceptional ease in yields of 90-95%. We synthesized a large number of derivatives with this method; some of them are given in Table 1.

A study of the chemical properties of the piazothiole derivatives synthesized by us revealed that the benzene ring in the heterocycle retains its aromatic character; the chlorination, bromination and thiocyanation of

TABLE 1

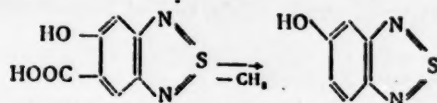
Diamine	Reaction Conditions		Product Obtained	M.p. in °C	Yield in %	N, %	
	Medium	Temp in °C	Time in hours			Found	Calculated
<i>o</i> -Phenylenediamine	Benzene, ethanol or methanol	60-80	0.5	44	85.92		
4-Tolylendiamine	Benzene or toluene	80-100	0.5	34	89		
1,2-Naphthylene-diamine	Toluene	100	1.5	80-81	98		
4-Nitrophenylene-diamine	Benzene, toluene, ethanol or methanol	60-100	1-3	127-128	84.5-90		
4-Ethoxyphenylene-diamine	Benzene	80	0.5	76-77	97.2		
Ethyl 3,4-diaminobenzoate	Toluene	100	2	57-58.5	95	13.31	13.4
3,4-Diaminobenzoic acid	Ethanol	80	1	225-226.5	90-95	15.05	14.95
3,4-Diaminobenzene-sulfonic acid	Aniline	120	3	melts above 300*	92.5	10.4	9.67
4-Chlorophenylene-diamine	Benzene	80	0.5	57.5	83.6	16.4	15.69
4-Bromophenylene-diamine	Toluene	100	0.5	59.5-61	69-90	13	12.42
3,4-Diaminobenzoic acid	Pyridine	60	1	212-213.5	85.7	14.2	13.82
3,3',4,4'-Tetraaminodiphenyl disulfide	Ethanol	60	0.5	121.5-122.5	98.8	16.65	16.94
3,4-Dichlorophenylene-diamine	Benzene	60	0.5	36-102 (not recrystallized)	98		
3,5-Dichlorophenylene-diamine	Benzene	60	0.5	97-97.5	98		
3,6-Dichlorophenylene-diamine	Benzene	80	0.5	178-179.5	86.16		
4,5-Dichlorophenylene-diamine	Benzene	80	0.5	109.5-110.5	88.6		
3,5-Dibromophenylene-diamine	Benzene or toluene	80-100	1-2	127	95-98		

* Also obtained by the oxidation of 2-methylnitrobenzene.

the 1- and 2-aminopiazothioles gave the corresponding mono- and dichloro, bromo, and thiocyno derivatives.

The reaction of ammonium thiocyanate with the hydrochlorides of either 1- or 2-aminopiazothiole gave the corresponding thiourea derivatives. Diazotization of the aminopiazothioles in sulfuric acid medium gave the corresponding hydroxypiazothioles.

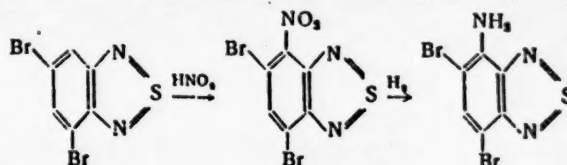
2-Hydroxypiazothiole was also obtained by the decarboxylation of 2-hydroxy-3-carboxypiazothiole:



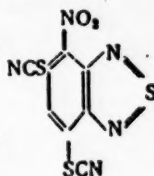
The corresponding thiocyanopiazothioles were obtained by the Sandmeyer reaction.

The indicated derivatives were converted by known methods into disulfides, aminosulfides, benzothiazole derivatives, ethers, etc.

Nitration of the obtained piazothiole derivatives gave the corresponding nitro compounds, which on reduction were converted into amines, as for example:



The mobility of the halogen group in the nitrohalo derivatives of piazothiole made it possible to synthesize certain compounds, the preparation of which by other methods would have presented considerable difficulties, as for example, 1-nitro-2,4-dithio- cyanotopiazothiole:



We also synthesized a number of organic phosphorus derivatives containing the piazothiole radical.

At the present time we are occupied in expanding the reactions developed by us for the interaction of thionylaniline and thionyl chloride with aromatic *o*-diamines to the aliphatic and heterocyclic series, and later we plan to study the physicochemical properties of the piazothiole derivatives obtained in this manner.

EXPERIMENTAL

Piazothiole. a) To a suspension of 5.42 g of *o*-phenylenediamine in 40 ml of benzene was added 15 g (12 ml) of thionylaniline; the mixture was heated on the water bath for 30 minutes and after removing the benzene by distillation the residue was acidified with dilute hydrochloric acid. The piazothiole, originally separating as an oil, crystallized; yield 6.2 g (91.18% of theory).

b) A mixture of 5.4 g of *o*-phenylenediamine, 20 g (27.5 ml) of triethylamine and 150 ml of benzene was treated under vigorous stirring with 15 g of thionyl chloride in 30 ml of benzene, the latter added gradually from a dropping funnel. The reaction proceeded with self-heating. Then the mixture was heated on the water bath for 15 minutes. The precipitate was filtered, washed with benzene, the filtrate evaporated, and the residue treated with water; the yield of piazothiole was 5.8 g (85.3% of theory).

2-Nitropiazothiole. a) A mixture of 1.5 g of 4-nitrophenylenediamine, 3.1 g (2.5 ml) of thionylaniline and 15 ml of benzene was heated under reflux for 3 hours. After cooling, the precipitate was suction-filtered, washed with 4% hydrochloric acid, and then with water; the yield of substance was 0.95 g. The filtrate, after removal of the benzene, was treated with 4% hydrochloric acid and then, the same as in the preceding, another

0.65 g of substance was obtained; the total yield was 1.6 g (88.8% of theory). After recrystallization from carbon tetrachloride the 2-nitropiazothiole had m.p. 127-128°.

b) To a mixture of 3 g of 4-nitrophenylenediamine and 7 g of pyridine in 100 ml of dichloroethane under vigorous stirring was gradually added a solution of 3.5 ml of thionyl chloride in 10 ml of dichloroethane, and then the mixture was heated on the water bath for 15 minutes. The resulting precipitate was filtered, washed with dichloroethane, the filtrate evaporated to dryness, and the obtained precipitate, after washing with water, was suction-filtered and worked up the same as the preceding; the yield of 2-nitropiazothiole was 3.1 g (84.7% of theory).

Preparation of thionylaniline. A solution of 13 g of thionyl chloride in 25 ml of ether was gradually added to a solution of 9.3 g of aniline and 15.8 g of pyridine in 100 ml of ether under vigorous stirring and over a period of 30 minutes; the reaction proceeded with self-heating. The resulting precipitate was filtered, washed with ether, and further the ether was distilled off; the yield of thionylaniline was 13.45 g (96.1% of theory).

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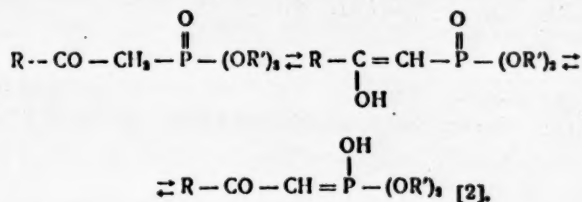
*T.p. = C.B. Translation pagination.

STUDY OF β -KETOPHOSPHINIC ACID ESTERS BY THE BROMINE TITRATION METHOD

Academician B.A. Arbuzov and V.S. Vinogradova

The classic example of tautomerism is that of keto-enol tautomerism, studied in detail on the esters of β -keto acids and other β -dicarbonyl compounds.

A comparison of the organic derivatives of phosphorus, containing the phosphono group, with the organic acids shows the deep analogy that exists between the phosphono group and the carboxyl group. Thus, according to the literature, there exists an analogy between the esters of the β -keto acids and the esters of the β -keto-phosphonic acids, which makes it possible for the indicated phosphorus derivatives [1] to show keto-enol tautomerism:

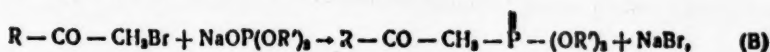
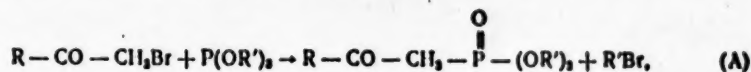


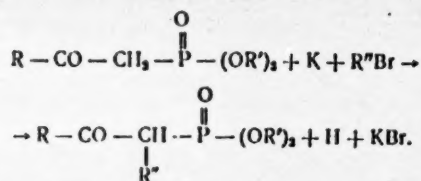
The data on the esters of the β -ketocarboxylic acids [3,4] fails to exclude the possibility of tautomerism also existing for compounds with a hydroxyl group on the phosphorus.

Direct data on the existence of enol forms for the esters of β -ketophosphinic acids and for the malonic ester analogs, those represented by phosphonoacetic ester, and especially on their number, fail to exist in the literature.

For the purpose of studying the problem of whether the enolic forms do exist for the β -ketophosphinic acid esters, and to compare the influence exerted by the carboxyl and phosphono groups on the ability to form the enolic forms, we synthesized earlier a number of β -ketophosphinic acid esters, both those described in the literature, and also some new compounds, and studied some of their properties [5].

It was possible to use the following methods for the synthesis of the indicated compounds: by the reaction of α -halocarbonyl compounds with the esters of phosphorous acid (the A.E. Arbuzov rearrangement) (Method A), by the reaction of α -halocarbonyl compounds with the salts of the dialkylphosphorous acids (the Michaelis-Becker reaction) (Method B), and by the alkylation of β -phosphonocarbonyl compounds, involving the treatment of their metallic derivatives with alkyl halides (Method C).



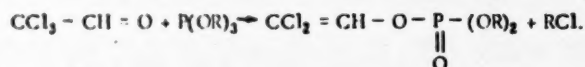


In the present communication we give the results obtained by us in studying the esters of β -ketophosphinic acids by the classic method of bromine titration developed by K. Meyer and involving the use of β -naphthol [6] (see Table 1). For comparative purposes the data on the enol contents, obtained by this method for similarly constructed carboxylic derivatives, are also given.

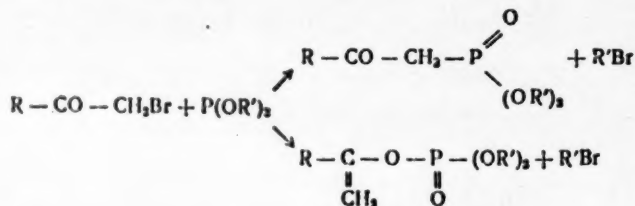
Together with the unsubstituted and monosubstituted β -ketophosphinic acid esters, we also synthesized the disubstituted derivatives, for which the existence of enol forms is impossible.

A comparison of the data in Table 1 shows that an analogy exists in the amount of enol, obtained by the bromine titration method, found for the phosphinic acid esters and for the corresponding carboxylic derivatives, but that there are also sharp deviations. Especially astonishing was the fact that some of the disubstituted derivatives, incapable of enolization, showed some unsaturation when titrated with bromine (dimethylphosphonoacetone 23%, phosphonomethylcyclohexanone 10%).

Perkow [7] showed that the reaction of chloral with trialkyl phosphites proceeds abnormally and leads to the formation of unsaturated esters of phosphoric acid:



In 1954, simultaneously with our studies, A.N. Pudovik [8] showed that this reaction can also proceed with α -halo ketones and, together with the normal reaction product, the unsaturated ester of the phosphoric acid can be formed:



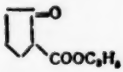
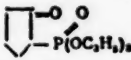
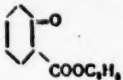
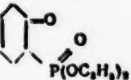
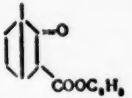
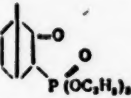
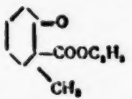
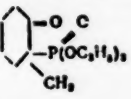
The amount of phosphoric ester formed depends on the reaction temperature and on the nature of the halide. A high temperature favors the formation of the ketophosphinic acid ester, a low temperature - the phosphoric ester. At times the chloro derivatives give almost exclusively the unsaturated phosphoric ester. The formation of the unsaturated esters of phosphoric acid explained the anomalous cases of unsaturation observed for the disubstituted derivatives.

The methylphosphonoacetone (No. 5 in Table 1) proved to be isomeric with the isobutenyl ester of the phosphoric acid. The methylphosphonoacetone isolated by us had the following constants: b.p. 92°/0.5 mm, d_4^{20} 1.0820, n_D^{20} 1.4342.

However, in other cases also, the amount of the enol form, found by the bromine titration method, could also be explained as being due to the presence of small amounts of difficultly removable unsaturated ester of the phosphoric acid.

Another method for the synthesis of the β -ketophosphinic acid esters is the Michaelis-Becker reaction, namely, the reaction of the sodium salt of diethylphosphorous acid with the corresponding haloketones. We synthesized a number of β -ketophosphinic acid esters by this method. The constants of the esters obtained in this manner differed somewhat from those of the same esters obtained via triethyl phosphite. For the case of

TABLE 1

Exp. Nos.	Substance	Enol, %	Substance	Unsaturation, %	Method
1	$C_6H_5OCO-CH_2-COOC_2H_5$	0	$C_6H_5OCO-CH_2-P(OC_2H_5)_2$	0	B
2	$C_6H_5OCO-CH(CH_3)-COOC_2H_5$	0	$C_6H_5OCO-CH(CH_3)-P(OC_2H_5)_2$	0	C
3	$C_6H_5OCO-C(CH_3)_2-COOC_2H_5$	0	$C_6H_5OCO-C(CH_3)_2-P(OC_2H_5)_2$	0	C
4	$CH_3-CO-CH_2-COOC_2H_5$	7.5	$CH_3-CO-CH_2-P(OC_2H_5)_2$	1.1	A
5	$CH_3CH_2-CO-CH_2-COOC_2H_5$	—	$CH_3CH_2-CO-CH_2-P(OC_2H_5)_2$	5.0	A
6	$CH_3-CO-C(CH_3)_2-COOC_2H_5$	0	$CH_3-CO-C(CH_3)_2-P(OC_2H_5)_2$	23	A
7	$C_6H_5CO-CH_2-COOC_2H_5$	21.4	$C_6H_5CO-CH_2-P(OC_2H_5)_2$	9.1	A
8	$C_6H_5-CO-CH(CH_3)-COOC_2H_5$	—	$C_6H_5-CO-CH(CH_3)-P(OC_2H_5)_2$	3.0	A
9	$C_6H_5CO-C(CH_3)_2-COOC_2H_5$	—	$C_6H_5CO-C(CH_3)_2-P(OC_2H_5)_2$	0	A
10		4.6		5.0	B
11		74.0		7.7	B
12		0.5		1.1	B
13		—		10	A

phosphonoacetone its substituted derivatives were obtained by the alkylation of its potassium derivative. A comparison of the constants for the preparations synthesized by the different methods is given in Table 2.

As can be seen, the obtained synthesis data and the bromine titration results do not permit answering the questions as to the presence of enolic forms and their number in the esters of various β -ketophosphinic acids. Further study of the α -ketophosphinic esters, by both chemical and physical methods, is required to obtain the desired answers.

TABLE 2

Substance	Method	B.p. in °C	Pressure in mm of Hg	d_4^{20}	n_D^{20}	Unsaturation
Phosphonoacetone	A	99-100	1.5	1.1574	1.4400	1.1
"	B	106-106.5	8.5	1.1127	1.4332	1.8
Diethylisopropenyl phosphate	—	107.5-109	18	1.0757	1.4200	81
Methylphosphonoacetone	A	92.0	0.5	1.0820	1.4342	••
"	B	108.0-110	8.0	1.0863	1.4350	3.0
"	C	115-116.5	6.0	1.0815	1.4368	1.0
Diethylisobutenyl phosphate	—	112-113.5	10	1.0602	1.4270	73.0
Dimethylphosphonoacetone	A	123-125.5	17	1.0518*	1.4293	21.0
"	B	103-103.5	5	1.0592*	1.4360	2.0
"	C	114	8	1.0645	1.4380	0.4
Phosphonoacetophenone	A	170-173	2.5	1.1650	1.5120	9.0
"	B	165	5	1.1615*	1.4990	7.2

* d_4^{20}

••The bromine titration failed to give stable results.

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STUDY OF THE SYSTEM $\text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{ZrO}_2$

Acad. Sci. USSR Corresponding Member P.P. Budnikov and A.A. Litvakovsky

The cast refractories prepared by electrical fusion have received widespread propagation both in the USSR glass industry and abroad, where they have also found successful use experimentally in metallurgy. At first they approached the mineral mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ in chemical composition and were chiefly composed of its crystals with a small amount of corundum crystals, a vitreous phase and impurities, the latter coming from the raw materials (bauxites, alites [1]). Then a small amount (5-7%) of zirconium dioxide was added, introduced as the concentrate obtained from the treatment of the mariupolites [2]. This addition proved to be beneficial for improving the crystal structure of the molten refractory.

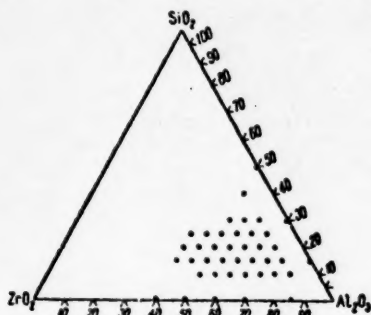


Fig. 1

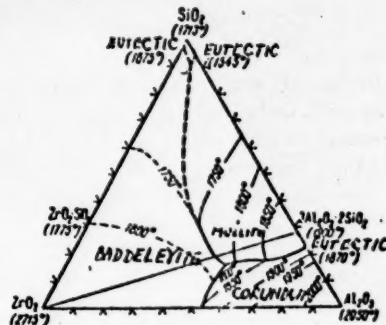


Fig. 2

Taking into consideration the favorable effect obtained in this manner, we undertook an extensive study of the aluminum oxide-rich portion of the system $\text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{ZrO}_2$, since the corresponding constitution diagram had apparently not been developed (it is absent in the literature). A construction of the corresponding portion of the equilibrium diagram on the basis of establishing the melting points and phase composition of a large number of mixtures should give a theoretical foundation to the technology of obtaining cast stone refractories with improved properties. With the aid of this diagram it becomes possible to establish the chemical composition of the charges that will favor the formation of cast refractories with the best phase compositions. We would like to mention that the obtained results, together with their scientific value, will also possess practical significance in those cases where the desired chemical compositions for the refractories can be obtained through the use of available raw materials.

The constitution diagrams of the binary systems $\text{Al}_2\text{O}_3 - \text{SiO}_2$ and $\text{ZrO}_2 - \text{SiO}_2$ are published in the literature [5], as are also the fusion diagrams of the systems $\text{ZrO}_2 - \text{Al}_2\text{O}_3$ [5] and $\text{ZrSiO}_4 - \text{SiO}_2 - \text{Al}_2\text{O}_3$ [6]. The $\text{Al}_2\text{O}_3 - \text{SiO}_2$ system was studied by Bowen and Greig [5], who found that only a single chemical compound, namely mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, was formed in it, which melted incongruently at 1810° . N.A. Toropov and F.Ya. Galakhov found [7] that mullite melts incongruently, since they established the presence of a temperature maximum (1870°) on the liquidus curve, in its position corresponding to the chemical composition of this compound, and they also found a eutectic (1850°) at a composition of 22.5% Al_2O_3 and 77.5% SiO_2 . P.P. Budnikov, S.G. Tresvyatsky and V.I. Kushakovskiy [8] confirmed the data of Toropov and Galakhov, and also obtained more accurate melting point values for the mullite (1900°) and eutectic (1870°). The equilibrium diagram was studied by Zhirnova [5], who found that ZrSiO_4 melts without decomposition (2430°). Later, George and Lambert [5]

established that zircon melts with decomposition under separation of monoclinic ZrO_2 . According to the latest data of Curtis and Saumen [5] zircon decomposes in the solid state at approximately 1540° into ZrO_2 and SiO_2 , and melts incongruently at 1775° , while a eutectic (1675°) exists in the system when the ZrO_2 content is under 3 mole %. According to von Wartenberg and Gurr [5], and von Wartenberg and Reusch [5], the minimum melting points for ZrO_2 - Al_2O_3 mixtures lie close to the ratio of 40 mole % ZrO_2 and 60 mole % Al_2O_3 . Geller, Yavonky, Steierman and Creamer [5], in studying the phase interrelationships that exist in the system BeO - Al_2O_3 - ZrO_2 , fixed a melting point of 1885° for the molar ratio Al_2O_3 : ZrO_2 = 1:1, i.e. 55 wt. % of ZrO_2 and 45 wt. % of Al_2O_3 . Rea [6] studied the fusion of ZrSiO_4 - SiO_2 - Al_2O_3 by the method of fixing the precipitation temperatures of the cones, prepared from the corresponding mixtures. As a result of this study it was established that a eutectic (1630°) exists between ZrSiO_4 and 20% Al_2O_3 , while a ternary point (1583°) was observed at 70% SiO_2 , 15% ZrSiO_4 and 15% Al_2O_3 .

As can be seen from our survey, for Al_2O_3 - SiO_2 - ZrO_2 mixtures the region of those rich in aluminum oxide has not yet been subjected to systematic study, although the best contemporary refractory materials are empirically prepared from mixtures that lie specifically in this region. Both existing studies [9] and practical data testify to the fact that the highest melting and most chemically stable compositions containing aluminum oxide, silica and zirconium dioxide are to be found among the ternary mixtures containing at least 50% of aluminum oxide. In connection with this we decided to study the melting points and phase compositions of the products obtained in the cooling of the molten mixtures, which mixtures contained from 95 to 50% of Al_2O_3 and from 5 to 50% of SiO_2 and ZrO_2 , in increments of 5%. In the process of doing this work it was shown possible to reject studying some of the indicated compositions, and instead, a supplementary study was made of some of the other compositions that proved of interest. A total of 40 mixtures of variable chemical composition were subjected to study (see Fig. 1).

In our study the batches of desired chemical compositions were mixed, molded with the aid of dextrin, and subjected to preliminary fusion in an electric arc. The melting points of the mixtures, prepared in the indicated manner, were determined in a microfurnace, designed by N.A. Toropov and F.Ya. Galakhov at the Institute of Silicate Chemistry of the Academy of Sciences of the USSR. This apparatus is described in the literature [7]. Essentially it consists of an electrically heated tungsten spiral inside the coils of which the studied sample, having a size of about 7-10 mm³, is placed on a tungsten wire. The furnace area, confined and isolated from the atmosphere by a glass dome (cover), is evacuated and then filled with argon that had been freed of impurities. The heating temperature of the sample is measured by the voltage applied to the spiral, which voltage is measured with a precision millivoltmeter. The point of incipient melting of the sample is determined visually, by observation through an optical assembly. After a definite holding time the specimen is cast on a water-cooled plate for hardening. The hardened specimens were studied petrographically, in which connection for obtaining a clear picture of the phase compositions and transitions the method of melting specimens of the same chemical composition at different temperatures and for various holding periods was used.* We estimate the accuracy of the melting point determinations obtained by us in the present study as being of the order of $\pm 20^\circ$. The study results are shown on that portion of the Al_2O_3 - SiO_2 - ZrO_2 constitution diagram that was developed by us (Fig. 2), for the construction of which we made partial use of the above-mentioned literature sources [5].

An examination of this ternary diagram shows the following:

The constitution diagram of the binary system Al_2O_3 - SiO_2 , as shown by Toropov and Galakhov, correctly expresses the reaction of these oxides in the region of high temperatures and high Al_2O_3 concentrations. The point for mullite lies in its own crystallization field (and not in the corundum field), in which connection the boundary curve between the mullite and corundum crystallization fields unites the point of the binary eutectic Al_2O_3 - SiO_2 (1870°) with the invariant point of the system Al_2O_3 - SiO_2 - ZrO_2 (1800°).

The relationship found to exist for the phases in the binary system Al_2O_3 - ZrO_2 does not support the interrelationships shown for them by Geller and other workers in the ternary phase diagram ZrO_2 - BeO - Al_2O_3 : the boundary between baddeleyite and corundum is established, not between 45 and 55 wt. % of Al_2O_3 , but instead between 50 and 60 wt. %.

Corundum proves to be the primary crystalline phase in the mixtures where the Al_2O_3 : SiO_2 ratio (by weight) exceeds 4:1.

*T.V. Bussen participated in the experimental work.

Baddeleyite becomes the primary crystalline phase in the region bounded by mullite when the ZrO_2 content in the mixtures exceeds 30%, and in the region bounded by corundum when the ZrO_2 content in the mixtures reaches 35%.

The invariant point, at which all three components of the given system show simultaneous crystallization at 1800°, roughly corresponds to a ratio of 53 wt. % of Al_2O_3 , 17 wt. % SiO_2 and 30 wt. % ZrO_2 (accuracy $\pm 2.5\%$).

An examination of the specimens, characterizing the crystalline structure of the cooled alloys, close in composition to the found eutectic, shows that they are all characterized by the same uniformly small dimensions for the crystals composing them. The presence of vitreous portions could not be shown in any of the examined specimens.

As the result of the present work it can be recommended that in selecting the chemical compositions of cast stone refractories, found within the limits of the system $Al_2O_3 - SiO_2 - ZrO_2$, that orientation be made around those quantities of these components that were found by us to correspond to the invariant point, i.e. Al_2O_3 53%, SiO_2 17% and ZrO_2 30%. Such a chemical composition for the refractory in ingot form assures the best crystallization character, inherent to eutectic mixtures, and namely, the obtaining of uniformly small crystals. This, in turn, will facilitate improvement in the corrosion resistance of the refractory and still give a sufficiently high melting point (1800°).

The present study indicates the reasonable maximum limit up to which it is practical to increase the amount of zirconium dioxide, being the most expensive component in the system, introduced into the composition of the aluminosilicate refractories, and here of exceeding importance is the fact that the required (30%) amount of ZrO_2 can be assured if zircon ($ZrSiO_4$), a mineral native to the USSR, is used.

The authors of this paper consider it their pleasant duty to thank F.Ya. Galakhov, Senior Research Associate of the Institute of Silicate Chemistry of the Academy of Sciences of the USSR, for his valuable services as a consultant in carrying out the present investigation.

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PREPARATION OF *p*-METHYLSTYRENE FROM UNSYMMETRICAL *p,p*-DITOLYLETHANE

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(Presented by Academician A.V. Topchiev, July 11, 1955)

Recently, a series of investigations [1-3] has been directed toward the problem of preparing styrenes from unsymmetrical diarylethanes. It has been established that, upon cracking, a molecule of unsymmetrical diarylethane is split, chiefly, into an alkylbenzene and the corresponding alkylstyrene. Thus, xylene and dimethylstyrene are obtained by cracking dixylylethane [3]. Cracking proceeds at temperatures of 400-600° in the presence of inert diluents and at contact times of the order of hundredths of a second. Certain mixed oxide catalysts and aluminosilicate clays are used as catalysts.

The preparation of styrenes by such a route can be of great interest if an effective means for the production of unsymmetrical diarylethanes is found and if cheap and active cracking catalysts are selected. In the above-cited work, the diarylethanes were synthesized by the condensation of aromatic hydrocarbons with acetaldehyde or by the alkylation of acetylene in the presence of sulfuric acid and mercuric sulfate according to the method of Reichert and Nieuwland [4]. The method is the more advantageous from the point of view of the starting materials, but the yields of diarylethanes do not exceed 50-60% of theoretical.

TABLE 1

Catalyst*	Conversion of DE into light products, %	Methylstyrene content in the 110-200*** fraction, %
Clay A	45.6	40.8
" B	49.7	38.3
" C	45.7	49.0
Aluminosilicate catalyst (Al ₂ O ₃ : SiO ₂ = 1:1)	59	48.0
Commercial aluminosilicate catalyst (Al ₂ O ₃ : SiO ₂ = 1:7)	70	26.9

* Clay A - bentonitic of unknown origin; Clay B - bentonitic clay from the "Askani" formation; Clay C - kudnovsky (submoscow) clay. The clays were activated by sulfuric acid treatment.

***The theoretical methylstyrene content of the light cracking products is 51.4%

The aim of the present work is to prepare *p*-methylstyrene from unsymmetrical *p,p*-ditolylethane and to study certain catalysts and cracking conditions.

The ditolylethane was prepared by the alkylation of toluene with acetylene in the presence of H₃PO₄·BF₃ + HgO, as the catalyst which, as shown by us earlier [5], is more active than sulfuric acid and mercury sulfate. Upon oxidation of the ditolylethane with chromic acid the sole oxidation product was terephthalic acid. Apparently, the ditolylethane consisted mainly of *p,p*-ditolylethane. It should be noted that ditolylethane synthesized

according to Reichert and Nieuwland contains only 10% *p,p*-ditolyethane [3].

The *p,p*-ditolyethane, which was distilled under vacuum several times, had the following basic constants: b.p. 139-140° (8 mm); d_4^{20} 0.9809, n_D^{20} 1.5670.

The cracking experiments were carried out in the apparatus shown in Figure 1.

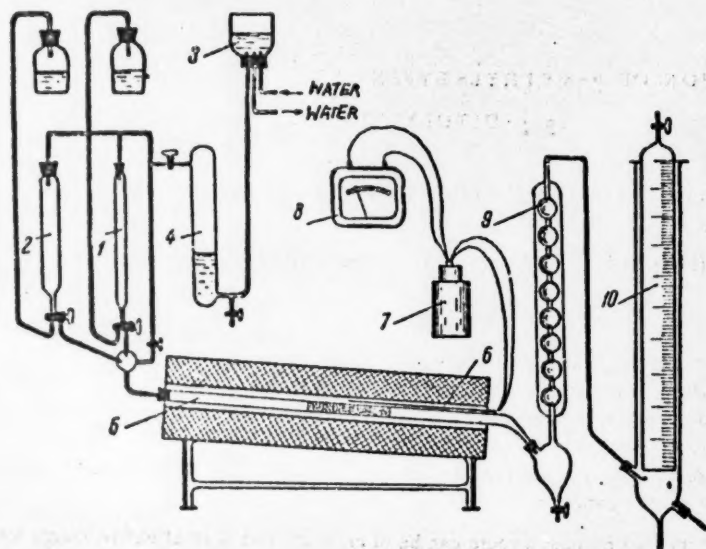


Fig. 1.

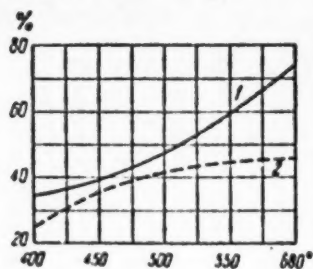


Fig. 2.

Fig. 2. Influence of temperature on ditolyethane conversion and methylstyrene content of the 110-200° fraction. Contact time 0.08 ± 0.01 seconds; molar dilution, moles H_2O /mole $C_{10}H_{18} \approx 70$. Catalyst - Clay A. 1 - Conversion of ditolyethane to light products, 2 - methylstyrene content of the 110-200° fraction of catalyzate.

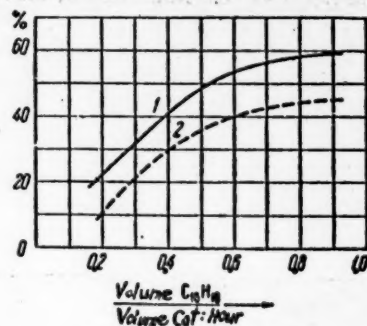


Fig. 3.

Fig. 3. Influence of space rate on ditolyethane conversion and methylstyrene content of the 110-200° fraction of catalyzate. Molar dilution, moles H_2O /mole $C_{10}H_{18} \approx 70$. Catalyst - Clay A. 1 - Ditolyethane conversion to light products, 2 - methylstyrene content of the 110-200° fraction.

Ditolyethane (DE) from buret 1 and water from buret 2, under the pressure of a column of water created by means of pressure vessel 3 and glass cylinder 4, flowed at a fixed rate into quartz catalyst tube 5 which was filled with catalyst and packing and was heated by an electric furnace. The amount of catalyst in all experiments was constant at 50 cc. The length of the catalyst tube was 16 cm. The temperature was measured by means

of chromelalumel thermocouple 6 and type XA millivolt meter 8 (7 is a Dewar flask). Steam and cracking products flowed to condenser 9; condensate drained into receiver, and uncondensed gas flowed to gasometer 10. The first experiment showed that very little gas is formed; in subsequent experiments it was not taken into account in the calculations. The catalyzate, an orange-colored liquid, was separated from the water dried with magnesium sulfate, and distilled at atmospheric pressure in the presence of hydroquinone as an inhibitor. In all cases, the catalyzate began to boil at 110°. The methylstyrene content of the fraction boiling at 110-200° was determined by the method of Rosenmund [6]. Five catalysts were tested: three aluminosilicate clays, a synthetic aluminosilicate catalyst ($\text{Al}_2\text{O}_3:\text{SiO}_2 = 1:1$), and a commercial aluminosilicate catalyst ($\text{Al}_2\text{O}_3:\text{SiO}_2 = 1:7$). All experiments were carried out at a temperature of $500 \pm 10^\circ$, a space rate of ditolyethane feed of 0.9 volumes DE/volume catalyst/hour, and with a molar dilution of the ditolyethane of 70 ± 2 moles H_2O /mole DE. The contact time was 0.08 ± 0.01 seconds.

The results are presented in Table 1.

From the table, it is seen that the best results were obtained with the synthetic aluminosilicate catalyst ($\text{Al}_2\text{O}_3:\text{SiO}_2 = 1:1$).

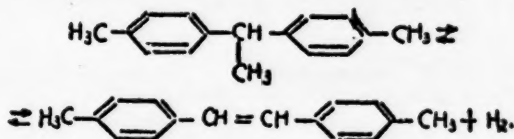
The curves (see Figures 2 and 3) show the dependence of ditolyethane conversion and of methylstyrene content of the 110-200° fraction on temperature and on space rate of ditolyethane feed.

The curves show that the conversion of ditolyethane to light products and the methylstyrene content of the 110-200° fraction increase with increasing cracking temperature (see Figure 2). At 600°, these values are 72 and 46%, respectively.

At temperatures above 600°, the character of the cracking changes sharply; thus, at 650°, instead of the usual liquid catalyzate, a large amount of solid crystalline material is obtained.

A decrease in the space rate of the feed (Figure 3) from 0.9 to 0.2 and the corresponding increase in contact time leads to a sharp decrease in conversion of ditolyethane into light products and to a decrease in the methylstyrene content of the 110-200° fraction. Besides the 110-200° fraction and unchanged ditolyethane, the catalyzate contained a crystalline substance which distilled at 175-180° (8 mm Hg), and which was identical with the product obtained at 650°. After several recrystallizations, the crystals melted at 179°, and were identified by us as *p,p*-dimethylstilbene (m.p. 180°). The molecular weight found by cryoscopic means was 210; the calculated molecular weight is 208.

The maximum quantity of *p,p*-dimethylstilbene was obtained at a feed space rate of 0.2 volumes DE/volume of catalyst/hour. Thus, an increase in the cracking temperature above 600° or a decrease in space rate of the feed leads to one and the same result — an increase in the stability of the *p,p*-ditolyethane toward cleavage and its transformation chiefly into *p,p*-dimethylstilbene:



The 110-200° catalyzate fractions from all of the experiments were poured together into one flask. After distilling off the toluene, the remainder was sealed in an ampoule where, over a period of three days at 120°, polymerization took place. The polymerization product, a thick, viscous liquid, contained residual toluene and, possibly, ethyltoluene and unpolymerized methylstyrene in addition to polymer. The contents of the ampoule were steam treated to free the polymer of all light material. The pure polymer was subjected to depolymerization under vacuum. The liquid product was distilled, and a plateau was reached at 50° at 8 mm Hg. The analytical results showed that the styrene obtained by us was *p*-methylstyrene.

The boiling point found was 50° (8 mm) (literature data, 51° at 9 mm). The molecular weight found was 120; calculated, 118. d_4^{20} found 0.8973 (literature value 0.8974). n_D^{20} found 1.5396 (literature value 1.5395). MR found 40.5; calculated 40.4.

*See reference [7].

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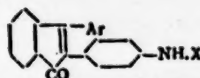
THE REDUCTION OF NITRO DERIVATIVES OF 2,3-DIARYL- AND 2-ARYL-3-ALKYLINDONES

Ch.P. Ivanov and B. V. Aleksiev

(Presented by Academician I. N. Nazarov, Nov. 26, 1955)

In a previous work [1] we studied the nitration of 2,3-diaryl- and 2-aryl-3-alkylindones. The aim of the present work was to study the reduction of nitroindones which would make it possible to prepare various indone derivatives, among them azo dyes.

TABLE 1

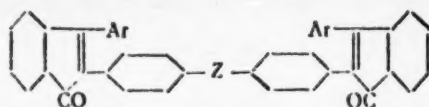


Ar	X	M.p. °C	Yield, %	N, %		Mol. wt.	
				Calculated	Found (by Kjeldahl)	Calculated	Found (by Rast)
C ₆ H ₅	H	186-187	96.4	4.71	4.65; 4.65	297.3	296.3
C ₆ H ₅	CO-CH ₃	185.5-186.5	96.6	4.13	4.00; 3.97	—	—
C ₆ H ₅	CO-C ₆ H ₅	221-222	92.6	3.49	3.38; 3.42	—	—
C ₆ H ₅	SO ₂ -C ₆ H ₄ -NH ₂ -CO-CH ₃	229-270	71.0	5.66	5.65; 5.70	—	—
C ₆ H ₅	SO ₂ -C ₆ H ₄ -NH ₂	220.5-221.5	68.0	6.19	6.14; 6.17	—	—
C ₆ H ₅ CH ₃	H	183-184	85.1	4.50	4.44; 4.48	311.4	312.3
C ₆ H ₅ CH ₃	CO-CH ₃	164-165	87.3	3.96	3.75; 3.81	—	—
C ₆ H ₅ CH ₃	CO-C ₆ H ₅	216-217	—	3.37	3.24; 3.25	—	—
C ₆ H ₅	H	110-111	80.3	5.62	5.58; 5.65	249.3	253.6
C ₆ H ₅	CO-CH ₃	140-141	91.5	4.81	4.70; 4.63	—	—
C ₆ H ₅	CO-C ₆ H ₅	185-186	—	3.96	4.13; 3.83	—	—
C ₆ H ₅	SO ₂ -C ₆ H ₄ -NH ₂ -CO-CH ₃	253-254	81.8	6.27	6.19; 6.17	—	—
C ₆ H ₅	SO ₂ -C ₆ H ₄ -NH ₂	268-269	41.0	6.93	6.87; 6.88	—	—

As is well known, reduction of nitro compounds to amines, without simultaneous reduction of an already existing carbon-carbon double bond, is accomplished by ferrous sulfate in an alkaline medium [2]. Although the activity of the double bond in nitroindones is higher due to conjugation with the carbonyl group, we obtained good results by this method. The first experiment was carried out with 2-*p*-nitrophenyl-3-phenylindone in ethyl alcohol saturated with ammonia. Dark cherry-red crystals of 2-*p*-aminophenyl-3-phenylindone were obtained in good yield. In addition, there were also isolated small quantities of neutral substances. By this same method, we prepared 2-*p*-aminophenyl-3-*p*-tolylindone from 2-*p*-nitrophenyl-3-*p*-tolylindone, and 2-*p*-aminophenyl-3-ethylindone from 2-*p*-nitrophenyl-3-ethylindone (see Table 1). A small quantity of neutral products was also obtained in these cases.

From the neutral materials obtained during the reduction of nitrodiphenylindone, dark red crystals melting at 254-255° were isolated by chromatography with aluminum oxide [3]. We attempted to increase their yield using ferrous sulphate under milder conditions. However, brick-red crystals melting at 225-226° were obtained by chromatography of the thus prepared neutral product. Upon oxidation of this product with hydrogen peroxide in acetone in an alkaline medium, the solution was decolorized, and a mixture of acids was obtained. Attempts at oxidation with lead dioxide [4] yielded only unchanged products.

TABLE 2

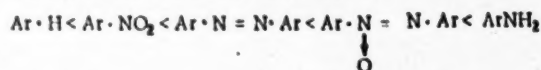


Ar	Z	M.p. °C	N, %		Mol. Wt.	
			Calculated	Found (by Kjeldahl)	Calculated	Found (by Rast)
C ₆ H ₅ C ₆ H ₄	-N=N- -N=N- O	254-255 225-226	4.74 4.62	4.77; 4.73 4.65; 4.69	590.6 606.6	597.4 601.1
C ₆ H ₅ CH ₂ C ₆ H ₄	-N=N- -N=N-	278-279 226-227	4.53 5.06	4.46; 4.41 5.41	618.7 —	637.5 —

duced no change in the crystals; only traces of aminodiphenylindone were formed. In view of the color, the melting point, the method of preparation of the crystals melting at 254-255°, and the results of the nitrogen and molecular weight determinations, it can be assumed that these crystals are an azodiphenylindone, more specifically, *p,p'*-bis-[2-(3-phenylindonyl)]-azobenzene. On the basis of the same considerations, we have assigned to the crystals melting at 225-226° the structure *p,p'*-bis-[2-(3-phenylindonyl)]-azoxybenzene (see Table 2).

The neutral product obtained during the reduction of nitrophenyltolylindone gave, upon chromatographing dark red crystals melting at 278-279°. On the basis of analogous considerations, it can be assumed that they are the corresponding azo compound — *p,p'*-bis-[2-(3-*p*-tolylindonyl)]-azo-benzene. In a similar manner, from the neutral product obtained during the reduction of nitrophenylethylindone we isolated dark orange crystals melting at 226-227°, to which we assigned, by analogy, the structure *p,p'*-bis-[2-(3-ethylindonyl)]-azobenzene.

As a result of the numerous experiments on the chromatographic separation and purification of the products obtained by the reduction of nitroindones, we established the following order of adsorption on aluminum oxide of diphenylindone and some of its nitrogen-containing derivatives:



We obtained in good yields the acetyl and benzoyl derivatives of the aminoindones. In view of the interest in colored sulfanilamides for the study of the metabolism of sulfanilamides in the organisms of microbes of higher animals, we prepared the sulfanilamides of aminodiphenylindone and aminophenylethylindone. Attempts to prepare the sulfanil derivative of aminophenyltolylindone gave resinous products from which, by chromatography, were isolated considerable quantities of aminophenyltolylindone and more difficultly eluted products which likewise did not crystallize.

Reduction of dinitrohydroxyhydrindone [1] under possibly milder conditions gives the same products as the nitroindones.

EXPERIMENTAL

1. Preparation of 2-*p*-aminophenyl-3-phenylindone. 1.000 g of 2-*p*-nitrophenyl-3-phenylindone was dissolved in 350 ml of ethyl alcohol, and the hot solution was saturated with ammonia. To the dark red solution thus obtained was added a hot solution of 9 g of crystalline ferrous sulfate in 50 ml of water saturated with ammonia. The mixture was boiled with stirring for an hour. The ferrous hydroxide was filtered off, the solution was concentrated, and, after dilution with water, it was extracted with ether. The dark cherry-red ethereal solution was extracted repeatedly with 18% hydrochloric acid. The yellowish orange hydrochloric acid solution was alkalinized. Extraction with ether yielded 0.866 g of lustrous dark cherry-red crystals (λ_{max} , 500 m μ) melting at 186-187°. They dissolved readily in benzene, acetone, and ethyl alcohol. They recrystallized from ether or 50% ethyl alcohol. 0.040 g of neutral material was isolated from the ethereal solution which had been ex-

Since the percentage of nitrogen in the neutral products expected from the reduction of nitrodiphenylindone was within experimental error, in order to clarify the structure of the products melting at 225-226° and 254-255° we attempted to establish their relationship. With this aim, we subjected the brick-red crystals melting at 225-226° to reduction using ferrous sulfate. Only dark red crystals melting at 254-255° were obtained by this means. A little aminodiphenylindone was isolated from the solution. An attempt to reduce the crystals melting at 254-255° using ferrous sulfate pro-

tracted with hydrochloric acid.

2. Preparation of 2-p-aminophenyl-3-p-tolylindone. By the same process, from 1,300 g of 2-p-nitrophenyl-3-p-tolylindone was obtained 0,813 g of dark red crystalline plates (λ_{max} , 495 m μ) melting at 193-194° and 0,087 g of neutral material.

3. Preparation of 2-p-aminophenyl-3-ethylindone. By this same method, from 1,000 g of 2-p-nitrophenyl-3-ethylindone was obtained 0,797 g of a dark red oil which, upon crystallization from petroleum ether, gave dark red crystals melting at 110-111°, 0,082 g of neutral material was isolated.

4. Preparation of azoxydiphenylindone. 0,500 g of nitrodiphenylindone was reduced as in the preparation of the aminoindones, but 2,7 g of ferrous sulfate was used, and the solution was heated only 10 minutes. There was obtained 0,251 g of neutral material which was dissolved in a mixture of petroleum ether and benzene (1:1) and subjected to chromatography with 11,0 g of aluminum oxide (activity of I on the Brockman scale). 0,022 g of neutral material was first eluted using this same solvent as the eluent; after this, using benzene as the eluent produced a broad rose-colored band which gave 0,179 g (38,5% yield) of brick-red crystals melting at 225-226° which were difficultly soluble in ethyl alcohol. (Orange crystals with the same melting point were obtained from acetone.) Further elution with benzene and ethyl alcohol yielded a brick red oil from which we were unable to isolate a crystalline product.

5. Preparation of azodiphenylindone. A. By reduction of azoxydiphenylindone. 50 mg of azoxydiphenylindone was dissolved in 180 ml of ethyl alcohol and reduced with 500 mg of ferrous sulfate by the method described under Experiment 1. After filtering off the solids and concentrating the filtrate, dark red crystals melting at 254-255° were isolated. The filtrate was treated as in the preparation of aminodiphenylindone. From the ethereal solution of neutral material was obtained a quite small quantity of the same crystals, and from the hydrochloric acid solution, there was isolated an insignificant amount (1,5 mg) of aminodiphenylindone which was identified by conversion to the acetyl derivative. The overall yield of dark red crystals was 46 mg (94,6%). They recrystallized well from benzene, acetone, or ethyl alcohol (solution in the latter was very difficult).

B. From the neutral product obtained during the preparation of aminodiphenylindone. By the chromatography of 200 mg of neutral product with 9,0 g of aluminum oxide (activity of I on the Brockman scale), as described in Experiment 4, there were eluted, successively, 4,5 mg of unchanged nitrodiphenylindone, 48,8 mg of azodiphenylindone (m.p. 254-255°), and resinous products from which we could not isolate any crystals.

6. Preparation of azophenyltolylindone. By chromatography of 200 mg of the neutral material obtained during the reduction of nitrophenyltolylindone, using 9,0 g of aluminum oxide (as in Experiment 4), 5,0 mg of unchanged nitrophenyltolylindone and 38,5 mg of dark red crystals melting at 278-279° (crystallized from ethyl alcohol) were isolated.

7. Preparation of azophenylethylindone. Upon chromatography of 200 mg of neutral material obtained by the reduction of nitrophenylethylindone, 63,0 mg of a brown resin was obtained; the resin, upon recrystallization from ethyl alcohol, gave dark orange crystals melting at 226-227°.

8. Preparation of 2-p-acetaminophenyl-3-phenylindone. 100 mg of aminodiphenylindone was dissolved in 10 ml of acetic anhydride and boiled for an hour, poured into water, heated 10 minutes at 50-60°, and extracted with ether. After evaporating of the ether, 109 mg of orange-red needles melting at 185,5-186,5° were crystallized from ethyl alcohol. By this same method, 110 mg of orange crystals melting at 164-165° (crystallized from alcohol) were obtained from aminophenyltolylindone, and 107 mg of yellowish brown crystals melting at 140-141° were obtained from aminophenylethylindone.

9. Preparation of 2-p-benzoylaminophenyl-3-phenylindone*. 200 mg of aminodiphenylindone was dissolved in 20 ml of acetone, 40 mg of sodium carbonate and 94 mg of benzoyl chloride were added, and the mixture was boiled about 1 hour. After the mixture was filtered, the acetone was evaporated off, and the remainder was recrystallized from ethyl alcohol. 250 mg of orange-red crystals melting at 221-222° were obtained.

By a similar method, dark red crystals melting at 216-217° (crystallized from alcohol) were obtained from aminophenyltolylindone, and brick-red crystals melting at 185-186° (crystallized from alcohol) were obtained from aminophenylethylindone.

10. Preparation of 2-(p-N-acetylsulfanilylaminophenyl)-3-phenylindone. 400 mg of aminodiphenylindone, 314 mg of N-acetylsulfanilyl chloride, 120 mg of sodium bicarbonate, and 50 ml of acetone were boiled 2 hours.

*The benzoyl derivatives of aminoindones were prepared by T. Ivanov.

472 mg of dark red crystals melting at 269-270° were isolated (crystallized from alcohol).

By a similar method, 293 mg of dark brown crystals melting at 253-254° were obtained from 200 mg of aminophenylethylindone (crystallized from methyl alcohol).

11. Preparation of 2-(p-sulfanilylamino-phenyl)-3-phenylindone. 100 mg of 2-(p-N-acetylsulfanilylamino-phenyl)-3-phenylindone was boiled for half an hour with 14% sodium hydroxide, neutralized, and the product filtered. 80 mg of brick-red crystals melting at 220.5-221.5° were crystallized from ethyl alcohol.

By a similar method, 37 mg of brown crystals melting at 263-269° were obtained from 100 mg of 2-(p-N-acetylsulfanilylamino-phenyl)-3-ethylindone (crystallized from methyl alcohol).

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CYANETHYLATION OF KETONES IN THE SYNTHESIS OF UNSATURATED LACTONES

δ -LACTONES WITH A HEPTACYCLIC DOUBLE BOND

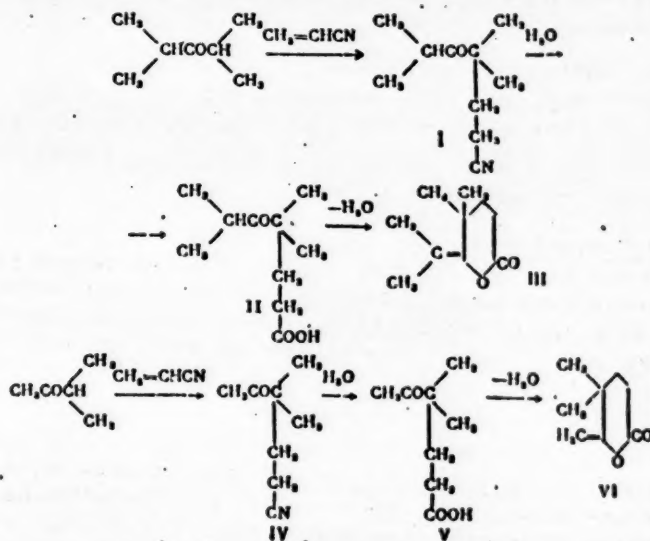
R.Ya. Levina, N.P. Shusherina, M.Yu. Lurye and N.D. Orlova

(Presented by Academician B.A. Kazansky, July 16, 1955)

Unsaturated δ -lactones with a heptacyclic double bond located near an oxygen atom have not been described in the literature, although these compounds are of interest from the point of view of their possible physiological activity.

For the synthesis of δ -lactones of such structure, we used in the present work the same route described by us earlier [1,2] for the preparation of unsaturated δ -lactones having the double bond in another position - cyanethylation of ketones, hydrolysis of the resulting nitriles into keto acids, and lactonization of the latter. Diisopropyl- and methyl isopropyl ketone were used as parent ketones.

The synthesis was carried out according to the following scheme:



The resulting lactones III and VI had heptacyclic double bonds, since their formation depended upon keto-enol rearrangement of the keto acids II and V, the enol forms of which are formed only because of the isopropyl group, in the first case, and the methyl group, in the second.

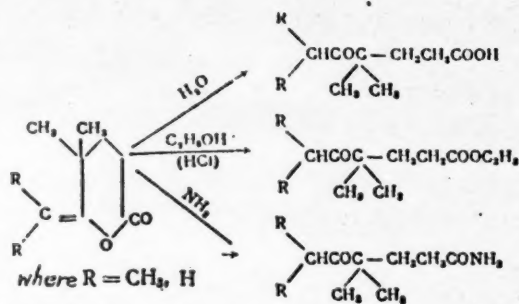
The parent ketonitriles I and IV were prepared by the reaction of the ketones with acrylonitrile in the presence of a 30% solution of potassium hydroxide in methanol. As revealed by the experiments, in the case of diisopropyl ketone the addition of a small quantity of the reaction product - monocyanethyated diisopropyl

ketone — into the reaction mixture increased the yield of product from 33 to 70%; according to literature data, this nitrile is obtained by cyanethylation of the ketone in a yield of 28% [3].

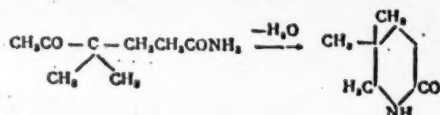
Study of the second stage of the synthesis — hydrolysis of the nitriles — showed that the nitriles are not hydrolyzed by dilute or concentrated hydrochloric acid; upon hydrolysis of the nitrile with a mixture of hydrochloric and acetic acids, the yield of the keto acid II reaches 46%. Excellent results were obtained with alkaline hydrolysis of the nitriles — yields of 86 to 97% were obtained.

Lactonization of the keto acids was carried out by warming with acetyl chloride; lactone VI (from keto acid V) was obtained with a yield of 85%, while the yield of lactone III (from keto acid II) was only 46%, apparently, due to steric hindrance.*

The resulting lactones with a heptacyclic double bond easily opened the lactone ring under the influence of water, alcohol (in the presence of hydrogen chloride), and ammonia with the formation of keto acids II and V, esters VII and VIII, and amides IX and X, respectively.



It was further shown that amide X is very easily transformed into the unsaturated lactam XI by heating or prolonged drying in a vacuum:



EXPERIMENTAL

Monocyanethylation of diisopropyl ketone (I) (γ -methyl- γ -isobutyrylvaleronitrile). To a mixture of 151 g (1.3 moles) of diisopropyl ketone, 2.5 ml of 30% methanol solution of potassium hydroxide, and 2 ml of γ -methyl- γ -isobutyrylvaleronitrile were added with constant stirring 16 g (0.3 moles) of acrylonitrile at a rate such that the temperature of the reaction mixture did not exceed 34–38°; stirring was continued for an additional 4 hours at room temperature. After distilling off the excess diisopropyl ketone, a yield of 38 g (70% yield) of γ -methyl- γ -isobutyrylvaleronitrile (I) was obtained; b.p. 124–126° at 8 mm; n_D^{20} 1.4428; d_4^{20} 0.9241; M_R found 47.95, calculated for $C_{10}H_{19}ON$ 48.21. Literature data: b.p. 128–129° at 10 mm; n_D^{20} 1.4435, d_4^{20} 0.9226 [3, 4].

γ -Methyl- γ -isobutyrylvaleric acid (II) and its ethyl ester (VII). 25 g (0.15 moles) of γ -methyl- γ -isobutyrylvaleronitrile was boiled with a solution of potassium hydroxide with stirring until the liberation of ammonia stopped; the reaction mixture was acidified with concentrated hydrochloric acid and extracted with ether. After the usual treatment, γ -methyl- γ -isobutyrylvaleric acid (24 g, 86% yield, not described in the literature) having the following properties was obtained; b.p. 156–157° at 10 mm; n_D^{20} 1.4500; d_4^{20} 1.0100; M_R found

*Steric hindrance also probably explains why we were unable to prepare semicarbazones from keto acid (II) and its ester (VII).

49.55, calculated for $C_{10}H_{18}O_3$ 49.92.

Found %: C 64.23; 64.03; H 10.01; 9.97
 $C_{10}H_{18}O_3$. Calculated %: C 64.42; H 9.74

The ethyl ester of γ -methyl- γ -isobutyrylvaleric acid (not described in the literature) was obtained in 72.5% yield by boiling a solution of the keto acid (7 g) in absolute ethanol (25 ml) with concentrated sulfuric acid (0.7 ml); b.p. 114-115° at 7 mm; n_D^{20} 1.4370; d_4^{20} 0.9532; MR_D found 58.89, calculated for $C_{12}H_{22}O_3$ 59.27.

Found %: C 66.88; 66.93; H 10.21; 10.48
 $C_{12}H_{22}O_3$. Calculated %: C 67.25; H 10.35

The unsaturated δ -lactone (III) from γ -methyl- γ -isobutyrylvaleric acid (5,5-dimethyl-6-isopropylidene-tetrahydro- α -pyrone). A mixture of 20 g of keto acid and 75 ml of acetyl chloride was boiled for three hours on a water bath. After vacuum distilling off the acetyl chloride, the residue was dissolved in ether, and washed with a cold soda solution (2 N) and water. 8 g (46.5% yield) of 5,5-dimethyl-6-isopropylidenetetrahydro- α -pyrone (not described in the literature) was obtained; b.p. 111-113° at 10 mm; n_D^{20} 1.4800; d_4^{20} 1.0112; MR_D found 47.26, calculated for $C_{10}H_{16}O_2$ 47.37.

Found %: C 70.98; 71.10; H 9.50; 9.46
Calculated %: C 71.40; H 9.46

During the lactonization of the γ -methyl- γ -isobutyrylvaleric acid, a substance having a b.p. of 192-194° at 8 mm and a m.p. of 58-60° (crystallized from aqueous alcohol) was formed along with the lactone; on standing in air, it was transformed into the original keto acid (n_D^{20} 1.4500; d_4^{20} 1.0100). Judging by the chemical properties and analytical data, this material was the anhydride of γ -methyl- γ -isobutyrylvaleric acid (not described in the literature).

Found %: C 67.93; 67.75; H 9.87; 9.60
 $C_{20}H_{34}O_8$. Calculated %: C 67.76; H 9.67

Alcoholysis of the lactone (III). A solution of 6.5 g of the lactone in 45 ml of absolute alcohol was saturated with gaseous hydrogen chloride. After the usual treatment, there was obtained 4 g (78% yield) of the ethyl ester of γ -methyl- γ -isobutyrylvaleric acid (VII) with the same constants as given above for this ester prepared from the keto acid.

Ammonolysis of the lactone (III). On shaking up the lactone with a concentrated aqueous solution of ammonia, there was obtained in 86% yield the amide of γ -methyl- γ -butyrylvaleric acid (IX) having a m.p. of 86-87° (crystallized from water).

Found %: N 7.85; 7.73
 $C_{10}H_{19}O_2N$. Calculated %: N 7.56

Literature data: m.p. 90° [5].

Monocyanethylation of methyl isopropyl ketone (IV) (γ -methyl- γ -acetylvaleronitrile). To a mixture of 21.5 g (0.25 mole) of methyl isopropyl ketone, 2.3 g of tertiary butyl alcohol, and 5.5 ml of a methanol solution of potassium hydroxide was added with stirring 15.9 g (0.3 mole) of acrylonitrile at a rate such that the temperature did not exceed 40°. The mixture was stirred for another 3-4 hours. Upon distillation of the reaction mixture, 15.6 (41.7% yield) of γ -methyl- γ -acetylvaleronitrile was obtained; b.p. 126-127° at 15 mm; n_D^{20} 1.4425; d_4^{20} 0.9451; MR_D found 39.08, calculated for $C_8H_{13}ON$ 38.97 (literature, b.p. 134° at 18 mm [6]).

γ -Methyl- γ -acetylvaleric acid (V) was obtained by hydrolysis of the nitrile according to the above-described method; b.p. 159-160° at 13 mm; m.p. 46-47°; yield 97%; (literature data: b.p. 160.5° at 13 mm; m.p. 48-49° [7]). Ethyl γ -methyl- γ -acetylvalerate was obtained by boiling a solution of the keto acid with absolute alcohol in the presence of sulfuric acid; b.p. 117-118° at 17 mm; n_D^{20} 1.4370; d_4^{20} 0.9790; MR_D found 49.83, calculated for $C_{10}H_{18}O_3$ 50.04. The m.p. of the semicarbazone of the ester was 77-78°.

Found %: N 17.67; 17.49
 $C_{11}H_{21}O_3N_3$. Calculated %: N 17.27

Literature data: b.p. 115-120° at 18 mm [8].

The unsaturated δ -lactone (VI) from γ -methyl- γ -acetylvaleric acid (5,5-dimethyl-6-methylenetetrahydro-

α -pyrone). A mixture of 7 g of the keto acid and 35 g of acetyl chloride was boiled for 3 hours. After the usual treatment, 5.5 g (85% yield) of 5,5-dimethyl-6-methylenetetrahydro- α -pyrone (not described in the literature) was obtained: b.p. 95-96° at 10 mm; n_D^{20} 1.4730; d_4^{20} 1.038; MR_D found 37.88, calculated for $C_8H_{12}O_2$ 38.13.

Found %: C 68.38; 68.59; H 8.59; 8.80
Calculated %: C 68.54; H 8.63

Hydrolysis of the lactone (VI). The lactone was gradually transformed into the original γ -methyl- γ -acetylvaleric acid by the moisture of the air. Titration with alkali of the lactone which had stood in air for several days revealed the presence of appreciable amounts of the acid. Upon standing in water at room temperature for 20 hours, 57-60% of the lactone was hydrolyzed (titration with alkali).

Alcoholysis of the lactone (VI) by the above-described method led to γ -methyl- γ -acetylvalerate (70% yield): b.p. 117° at 16-17 mm; n_D^{20} 1.4372. The semicarbazone of the ester melted at 77-78°. A test on a mixture of two preparations of semicarbazone showed no depression of melting point.

Ammonolysis of lactone (VI) was carried out as described above for lactone (III). The amide of γ -methyl- γ -acetylvaleric acid, after four-fold recrystallization from ethyl acetate, melted at 113-115°. The amide dissolved easily in water and alcohol, poorly in ether. No depression of the melting point was obtained when this amide was mixed with one prepared by ammonia treatment of ethyl γ -methyl- γ -acetylvalerate.

Found %: N 8.83; 9.04
 $C_8H_{15}O_2N$. Calculated %: N 8.83

Amide (X) was easily transformed by heating into lactam (XI) - 5,5-dimethyl-6-methylenepiperidone, m.p. 108-109° (crystallized from water). Splitting out of water and formation of the lactam also proceeds upon drying the amide in a vacuum.

Found %: N 10.02; 10.11
 $C_8H_{13}ON$. Calculated %: N 10.01

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CHROMATOGRAPHIC SEPARATION OF ISOMERIC $C_8H_{18}S$ ORGANIC SULFUR COMPOUNDS BY USING RADIOACTIVE SULFUR

P.D. Obolentsev, B.V. Alvazov and S.V. Netupskaya

(Presented by Academician A.V. Topchlev, July 1, 1955)

In recent years the chromatographic method has begun to be used for studying the organic sulfur compounds that are found in petroleum and petroleum products. However, up to now, the number of studies devoted to this problem have been comparatively few. I. Ya. Postovsky, N.P. Bednyagina and M.A. Mikhailova [1] were the first to indicate the possibility of isolating organic sulfur compounds from petroleum by chromatographic separation. Haresnape, Fidler and Lowry [2] showed that mixtures of sulfides, disulfides, and thiophene could be separated chromatographically on silica gel. Karr and coworkers [3], who subjected some petroleum crudes, deposited on aluminum oxide, to chromatographic development, were able to isolate the organic sulfur compounds that were present as concentrates. Thompson and coworkers [4], who identified 43 organic sulfur compounds in the benzine fraction of a Texas petroleum crude, used the method of chromatographing on silica gel in their investigation.

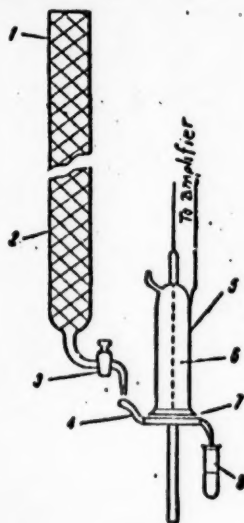


Fig. 1. 1 Diagram of chromatographic apparatus with an end-window counter, 1 - chromatographic column, 2 - adsorbent, 3 - stopcock, 4 - small lead pipe, 5 - counter, 6 - counter thread, 7 - mica window, 8 - 1 ml test tube.

In view of the fact that isomeric organic sulfur compounds are contained in petroleum fractions, it appeared of interest to elucidate in principle the possibility of their chromatographic separation, especially since this problem had failed to receive illumination in the literature that was available to us. For this reason we set ourselves the task of executing this work. As study subjects we selected the isomers: *n*-octyl mercaptan, di-*n*-butyl sulfide and diisobutyl sulfide, i.e., compounds having the molecular formula of $C_8H_{18}S$, and whose boiling points lie within the boiling range of the ligroin fraction in petroleum.

Due to the absence of any other reliable methods for controlling the yield of the isomeric sulfides in the chromatographed filtrates we used the method of labeled atoms. For this purpose we synthesized diisobutyl sulfide, labeled with radioactive sulfur-35. The compound was synthesized by the semimicro method, starting with isobutyl bromide and radioactive sodium sulfide. The diisobutyl sulfide obtained in this manner had b.p. 84-85° at 30 mm of Hg pressure; d_4^{20} 0.8270; n_D^{20} 1.4470; its specific activity by the end-window counter was 3400 impulses/min. g. The di-*n*-butyl sulfide, synthesized from normal butyl bromide and sodium sulfide, had b.p. 83° at 16 mm of Hg pressure; d_4^{20} 0.8385; n_D^{20} 1.4525. The *n*-octyl mercaptan, synthesized from normal octyl bromide and sodium thiosulfate with subsequent acid hydrolysis, had b.p. 82° at 16 mm of Hg pressure; d_4^{22} 0.8430; n_D^{22} 1.4530.

The chromatographic separation was run in glass columns (diameter 10 mm, height 500 mm), filled with silica gel of MSM grade and having a particle size of 0.5-0.25 mm. An end-window 8-counter

with a mica window, making it possible to realize continuous direct control of the filtrate yield from the column, was prepared for determining the amount of radioactivity in the chromatographed filtrates. After issuing from the column the chromatographed filtrates flowed directly under the window of the end-window counter. A diagram of this apparatus is shown in Fig. 1. The appearance of the radioactive sulfide in the filtrate (concentration of about 0.01%) was easily detected by the counter, the reading of which was recorded every minute.

TABLE 1

Results of the Chromatographic Elution of a Mixture of Di-*n*-butyl Sulfide and Diisobutyl Sulfide With Binary Mixtures

Acetone concentration in the binary mixture in volume %								
6.25			10.00			50.00		
Vol- ume, ml	S, %	imp- ulses/ /min.	Vol- ume, ml	S, %	imp- ulses/ /min.	Vol- ume, ml	S, %	imp- ulses/ /min.
0	0,0	0	0	0	0	0	0	0
55	0,02	0	28	0	0	3	0,01	0
56	0,20	125	29	0,22	120	5	1,17	503
58	0,32	198	30	0,48	250	7	0,85	480
63	0,48	250	31	0,52	262	9	0,15	98
65	0,31	226	32	0,56	270	11	0,06	40
66	0,08	110	33	0,72	431	13	0,06	25
68	0,00	0	34	0,55	262			
70	0,00	0	38	0,17	100			
72	0,00	0	40	0,00	0			
74	0,00	0						
76	0,00	0						
78	0,00	0						
80	0,00	0						

For chromatographing there were taken: 1) *n*-octyl mercaptan and diisobutyl sulfide; 2) di-*n*-butyl sulfide and diisobutyl sulfide; 3) *n*-octyl mercaptan, di-*n*-butyl sulfide, and diisobutyl sulfide, dissolved in the desulfurized fraction from Tulumaza petroleum and boiling in the range 200-215°. In each experiment 15 ml of the corresponding solution was poured on the silica gel and then eluted with either binary mixtures (acetone-isooctane) or with the ternary mixture (acetone 6.25 vol. %, benzene 31.25 vol. %, and isooctane 62.50 vol. %). The acetone content in the binary mixtures ranged from 6.25 to 50 vol. %.

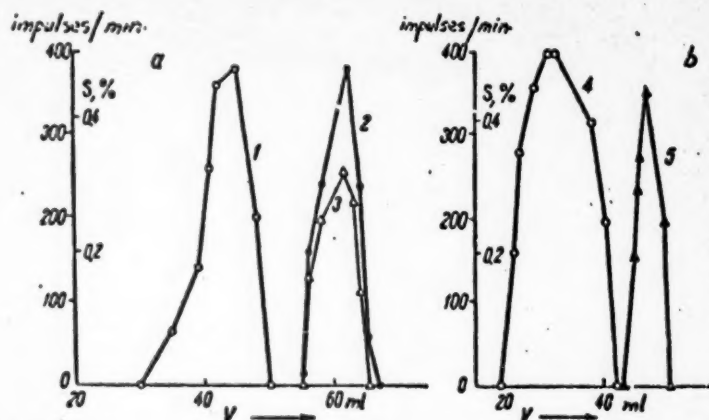


Fig. 2. 1 a) chromatogram of a mixture of *n*-octyl mercaptan, di-*n*-butyl sulfide and diisobutyl sulfide; eluent - acetone (6.25%) with isooctane (93.75%); b) chromatogram of a mixture of di-*n*-butyl sulfide and diisobutyl sulfide; eluent - acetone (6.25%), benzene (31.25%) and isooctane (62.5%). 1) $C_8H_{17}SH$; 2) $(HC_4H_9)_2S + (i-C_4H_9)_2S$; 3) $(i-C_4H_9)_2S$; 4) $(HC_4H_9)_2S$; 5) $(i-C_4H_9)_2S$

The experimental results on the chromatographic elution of the mixture of normal and isobutyl sulfides with binary mixtures are given in Table 1. The volumes of the chromatographed filtrates and their corresponding concentrations of eluted substances, expressed in weight percents of sulfur and in impulses per minute (after subtracting the ground), are indicated in this table.

From an examination of the data in Table 1 it follows that the chromatographic elution of the mixture of normal and isobutyl sulfides with the binary acetone-isooctane mixtures, in the acetone concentration limits studied by us, failed to permit the separation of the mixed isomeric sulfides with an empirical formula of $C_8H_{18}S$. As can be seen from the data in Table 1, the values of the maxima on the yield curves (heavy type numbers), obtained by the method of lamp sulfur determination, coincide with the maxima, obtained by the method of measuring the radioactivity of the chromatographed filtrates. This means that both di-n-butyl sulfide and diisobutyl sulfide are eluted simultaneously from the chromatographic column.

The results of one of the experiments on the chromatographic elution of a mixture of n-octyl mercaptan, di-n-butyl sulfide and diisobutyl sulfide with a binary mixture of acetone (6.25%) and isooctane (93.75%) are given in Fig. 2 a. From an examination of this figure it follows that elution with the binary mixture permits isolating n-octyl mercaptan from its mixture with normal and isobutyl sulfides, i.e. in this case it became possible to separate the isomers of empirical formula $C_8H_{18}S$, but belonging to different groups of organic sulfur compounds.

We achieved the chromatographic separation of a mixture of di-n-butyl sulfide, and diisobutyl sulfide by the method of eluting it with the ternary mixture of acetone, benzene and isooctane. The results of one of these experiments are shown in Fig. 2 b. The curves, depicted in this figure, clearly demonstrate the possibility of chromatographic separation for a mixture of two isomeric sulfides belonging to the aliphatic series.

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STUDY OF THE SYSTEM NI-S FROM 30.0 TO 50.0 ATOMIC % S

M. A. Sokolova

(Presented by Academician G.G. Urazov, May 10, 1955)

The system Ni-S was studied by Bornemann [1,2]. The β -phase and the compound Ni_3S_2 were found by this author and the formation of the compound Ni_5S_3 was postulated. Alsen [3] determined the cubic structure of Ni_3S_2 by the x-ray method. Later, Westgren [4] determined the structure of Ni_3S_2 more accurately and showed that its structure is not cubic, but instead is rhombohedral. Biltz [5] established two modifications for NIS. The compound NIS was also obtained by Kolkmeijer and Moseveld [6]. Levi and Baroni [7] indicate three modifications for NIS: α -NIS - amorphous, β -NIS - high temperature modification, and γ -NIS - low temperature modification. Peyronel and Pacilli [8] confirmed the compound Ni_3S_2 , two NIS modifications, and found a phase (31.9-32.0 wt % of S) to which they assigned the composition Ni_7S_4 . Lundqvist [9] established the existence of two phases between the compounds Ni_3S_2 and NIS: Ni_5S_3 exists above 400° and Ni_7S_4 exists below 400° . The system Ni-S was studied by a number of authors [1-9].

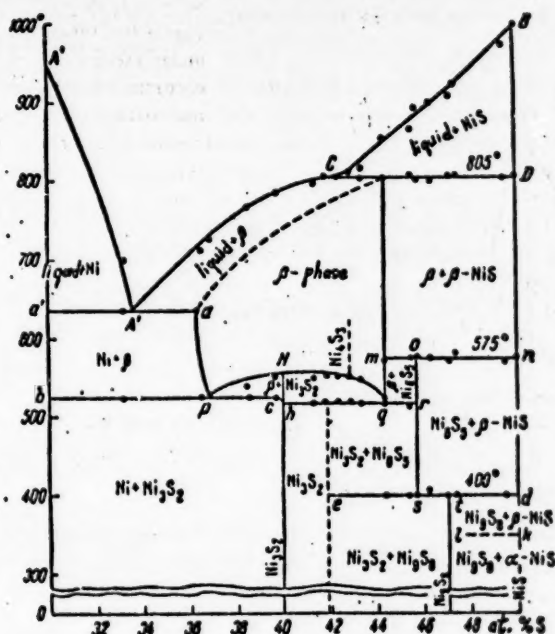


Fig. 1. Constitution diagram of the Ni-S system.

We studied the system Ni-S in the concentration interval of 30.0 to 50.0 at. % of S (19.0-35.3 wt. %) by the following methods: thermal, microstructure, x-ray, flow pressure, electrical conductivity, and specific gravity.

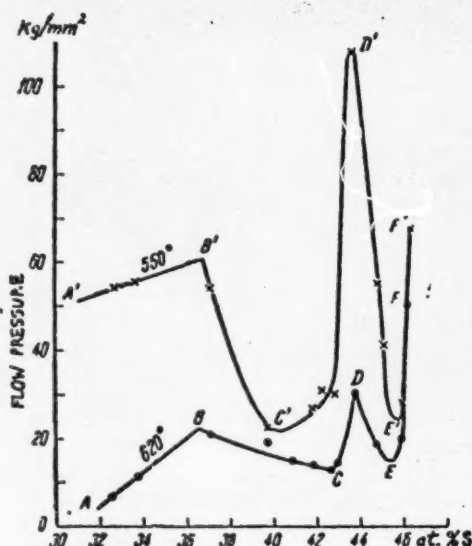


Fig. 2. Flow pressure curves of Ni-S alloys at 620 and 550°.

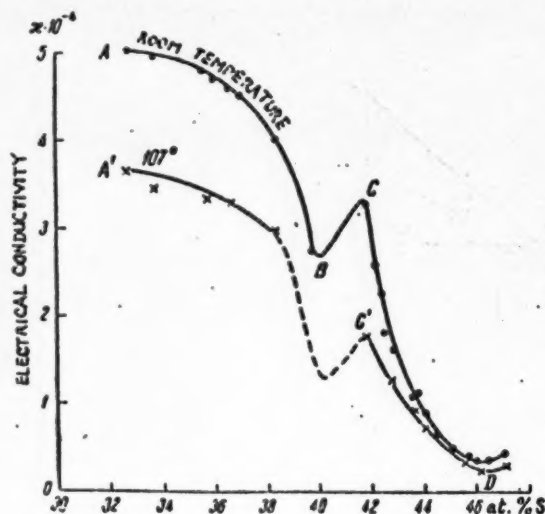


Fig. 3. Electrical conductivity curves of cast Ni-S alloys.

crystallization of metallic nickel. The primary β -phase separations occur along the curve AC . The curve CB corresponds to the primary NiS separations. Along the straight line CD at 805° the β -phase of a compound of variable composition is formed in accord with the peritectic reaction: $NiS + \text{melt} \rightleftharpoons \beta\text{-phase}$. The straight line $a'a$ (635°) corresponds to the crystallization of the eutectic: $Ni + \beta\text{-phase}$. Along the curve $pliq$ with a maximum at 550° the compound Ni_3S_2 is formed as the result of β -phase decomposition. The straight lines bpc (525°) and hqr (518°) correspond to eutectoid decomposition; at point p the decomposition proceeds by the reaction: $\beta\text{-phase} \rightleftharpoons Ni + Ni_3S_2$; at point q by the reaction: $\beta\text{-phase} \rightleftharpoons Ni_3S_2 + Ni_5S_8$.

The compound Ni_5S_8 is formed as a solid along the straight line mon at 575° in accord with the reaction: $\beta\text{-phase} + NiS \rightleftharpoons Ni_5S_8$. The straight line $estd$ (400°) corresponds to decomposition of the compound Ni_5S_8 with the formation of a compound having a composition close to that of Ni_3S_2 . The dotted line lk at 350° corresponds

The alloys of nickel with sulfur were prepared by two methods: in graphite crucibles and in quartz test tubes sealed under vacuum. The melts in the open crucibles were prepared in a crypt furnace by the method of throwing pieces of sulfur and metallic nickel into a red-hot graphite crucible. After saturation with sulfur the melts were drawn by suction into rods in heated porcelain tubes having a diameter of 3-4 mm. The maximum amount of sulfur obtained in the melts by this method was 47.25 at. % of S (33.0 wt. %), after which the alloy was covered with charcoal and kept in the furnace. Here the sulfur was burned out of the alloy, and after definite time intervals the rods were drawn by suction from the previously mixed alloy.

The alloys containing more than 47.25 at. % of S (33.0 wt. %) were prepared by the powder fusion method. The powdered metallic nickel and sulfur were well mixed and then fused in quartz test tubes that had been sealed under vacuum. Ni-S alloys containing up to 36.0 wt. % of S were prepared in this manner. The composition of the obtained alloys was established by analysis.

In the thermal study the heating and cooling curves of the alloys were obtained in quartz vessels using the N.S. Kurnakov differential recording pyrometer and Pt/PtRh thermocouples.

The thermal analysis results are shown in Fig. 1. Conjointly with the results of all of the methods used in studying the Ni-S system, the phase diagram is interpreted in the following manner. Curve $A'A$ corresponds to the

to the polymorphous transformation of the high-temperature modification of NiS into the low-temperature modification.

The Ni-S alloys, cooled with the furnace and hardened from 600°, were studied by the microstructure method. The microstructure study showed the presence of three compounds in the system: Ni_3S_2 , Ni_5S_3 , NiS.

The cast alloys, hardened from 600° and annealed at 380 and 200°, were also studied by the x-ray method. The x-ray study of the Ni-S alloys supported the formation of compounds Ni_3S_2 , Ni_5S_3 and two modifications of the compound NiS. The compound of composition Ni_4S_3 , proposed by Peyronel and Pacilli [8], and by Lundqvist [9], fails to exist. According to our data there does exist a compound, in composition close to that of Ni_4S_3 , that is formed in the solid state at 400° and can be seen in the pure form in the alloys annealed at 200°. The phase Ni_5S_3 is easily hardened and decomposes very slowly at 400°. We reject the postulation made by Lundqvist [9] on the peritectic formation of this phase. The phase Ni_5S_3 is formed at 575° in accord with the reaction: $\beta\text{-phase} + \beta\text{-NiS} \rightleftharpoons \text{Ni}_5\text{S}_3$. The high-temperature NiS β -modification with hexagonal structure of type NiAs is easily hardened and at 350° is slowly converted as a solid into the low-temperature α -modification with a rhombohedral structure of the millerite type. To confirm the existence of the high-temperature β -phase a study was made of the flow pressures at 550 and 620°. The flow pressure curves are shown in Fig. 2, which curves have two maxima at B and D and two minima at the points C and E. In accord with the constitution diagram for the Ni-S system it can be assumed that the two maxima correspond to the boundaries of the β -phase with the two-phase regions. The minima correspond to compositions of compounds. The portion BCD on the ABCDE curve at 620° relates to the β -phase with a minimum at point C, corresponding to the composition of the compound Ni_4S_3 (42.86 at. % of S). Minimum E corresponds to the compound composition Ni_5S_3 (45.45 at. % of S). The flow pressure curve, obtained at 550°, also has two maxima B' and D' and two minima C' and E'. The maxima at points B' and D', and also the minimum at E', correspond to the same values as for the curve at 620°. The second minimum C', in accord with the constitution diagram, corresponds to the composition of the compound Ni_3S_2 .

The cast Ni-S alloys, and also those annealed at 380°, were studied by the electrical conductivity method. The cast alloys were studied on a Thompson double bridge at room temperature and at 107°. Because of the brittle nature of the specimen, the electrical resistance of the alloy with a composition close to that of the compound Ni_3S_2 could not be measured at 107°.

The electrical conductivity curves of the cast Ni-S alloys are shown in Fig. 3. On the electrical conductivity curve at room temperature the minimum B corresponds to the compound Ni_3S_2 . The sloping minimum at point D makes it difficult to assign any definite phase to it, since it embraces the region from 45.0 to 47.0 at. % of S. The maximum at point C with an S content of 4.18 at. % corresponds to the boundary of the one-phase region with the two-phase region. The electrical conductivity study results for the cast alloys at 107° (Fig. 3) show that the alloys, rich in nickel, possess a lower electrical conductivity at 107° than at room temperature. The alloys, richer in sulfur, possess nearly the same electrical conductivity at 107° that they do at room temperature. The electrical conductivity curve of the alloys annealed at 380° is similar to the electrical conductivity at room temperature, except that the second minimum is more clearly delineated and in composition approaches that of the compound Ni_5S_3 . The electrical conductivity curves in Fig. 3 show that the nickel-rich alloys possess metallic conductivity. In the magnitude of their electrical conductivity the sulfur-rich alloys resemble the semiconductors. It is a known fact that the semiconductors possess a lower electrical conductivity for the pure substances than for mixtures. We also see a similar relationship in Fig. 3.

A smooth curve was obtained for the specific gravities of the Ni-S alloys, which shows that the specific gravity of the alloys decreases with increase in the amount of sulfur in the alloys.

SUMMARY

The following phases were established in the system Ni-S:

- 1) A high-temperature β -phase with a region of homogeneity from 36.20 to 43.60 at. % of S at 635°, formed by the peritectic reaction at 805°: $\text{NiS} + \text{melt} \rightleftharpoons \beta\text{-phase}$. It was shown that the β -phase can be regarded as being a solid solution based on the compound Ni_4S_3 , and which is not retained by hardening.
- 2) The phase Ni_5S_3 is formed at 550° due to decomposition of the β -solid solution.

*Together with V.G. Kuznetsov.

3) The phase Ni_3S_2 is formed in the solid state at 575° as the result of the reaction: $\beta\text{-phase} + \text{NiS} \rightleftharpoons \text{Ni}_3\text{S}_2$. The compound Ni_3S_2 is retained by hardening and decomposes very slowly at 400° with the formation of the phase Ni_3S_4 .

4) The phase Ni_3S_4 is obtained in the solid state at 400° as the result of the reaction: $\text{Ni}_3\text{S}_2 + \text{NiS}$. This phase was established by the x-ray method as being present in the specimens annealed at 380 and 200° .

5) The existence of the compound NiS in two modifications was confirmed.

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STUDY OF THE REACTION OF AMMONIA WITH THE HALIDES OF DIVALENT METALS IN AQUEOUS MEDIUM

THE SOLUBILITY OF CADMIUM CHLORIDE IN AQUEOUS AMMONIA SOLUTIONS

Academician G.G. Urazov and A.K. Kirakosyan

The system composed of cadmium chloride, ammonia and water, in the entire range of ammonia concentrations and at definite temperatures, has failed to be systematically studied. Most of the papers given in the literature on the study of the reaction of ammonia with cadmium chloride deal with the synthesis of the ammoniates of cadmium chloride and their thermal stability.

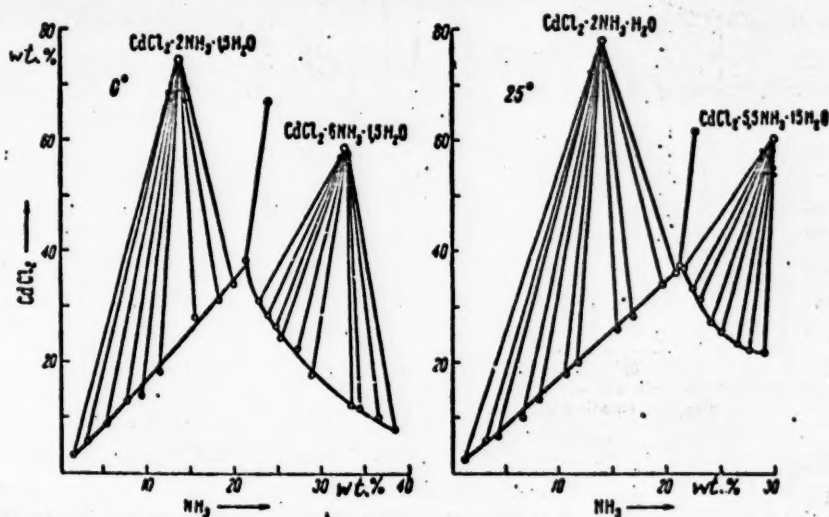


Fig. 1. Solubility isotherms of the system $\text{CdCl}_2 - \text{NH}_3 - \text{H}_2\text{O}$ at 0 and at 25°

Anhydrous cadmium hexammine chloride was obtained by the passage of gaseous ammonia through anhydrous cadmium chloride [1-3]. The dissociation pressures of these compounds at various temperatures were determined [2,4,5]. The behavior patterns of the intermediate dissociation products of the hexammine were studied [4,6].

Cadmium diammine chloride was obtained by various methods, both by the addition of cadmium chloride to aqueous ammonia solutions, and by the dry method [6-8]. The thermal properties of cadmium diammine chloride were studied and its heat of formation was determined [4,8,9].

Cadmium monoammine chloride was obtained by the distillation of the diammine chloride [7]. Its dissociation pressure [4] and heat of dissociation [5] were determined.

EXPERIMENTAL

It is known that the reaction between ammonia and cadmium salts proceeds in two stages: with a definite amount of ammonia in the solution the hydroxides of variable composition (basic salts and hydroxy ammoniates) are first deposited, and then, beginning with definite concentrations of ammonia in the solution, these hydroxides dissolve, and further ammonia addition leads to salting out of the ammoniates. Due to the absence of exchange reaction in the last reaction stage for systems composed of cadmium salts, in the given case cadmium chloride, ammonia and water, these systems can be regarded as being ternary in nature.

The isothermal solubility method was used to study the reaction between cadmium chloride and ammonia in aqueous medium. The region of crystallization for the hydroxide precipitates was studied at 25°, while the region of crystallization for the ammoniates was studied at 0 and 25°. In studying the crystallization region of the hydroxide precipitates we started with dilute aqueous ammonia solutions, dissolving cadmium chloride in them until precipitates were formed. In studying the crystallization region for the ammoniates we proceeded from cadmium chloride solutions, passing gaseous ammonia into them until crystalline precipitates were obtained. The mixtures prepared from the region of crystallization for the ammoniates were kept in a thermostat for 6-8 hours with frequent stirring, while from the region of crystallization for the hydroxide precipitates the mixtures were kept for 20-25 days. The liquid and solid phases from both regions of the system were analyzed for their Cd^{2+} content as $\text{CdSO}_4 \cdot \text{Cl}^-$ was determined by titration with silver nitrate solution, and OH^- and NH_3 were determined by direct titration with sulfuric acid.

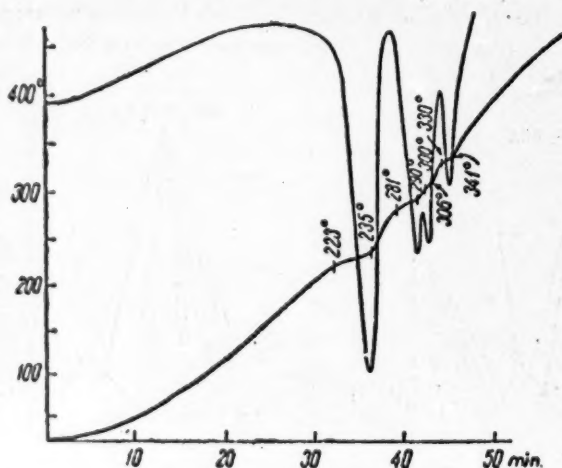


Fig. 2. Heating curves of $\text{CdCl}_2 \cdot 2\text{NH}_3$.

In its size the crystallization region for the hydroxide precipitates is small, and is characterized by the fact that its solid phases are ammonia-containing formations of variable composition, despite the low ammonia concentration present in the corresponding equilibrium liquid phases. The deposition of hydroxide precipitates of general composition $n\text{CdCl}_2 \cdot m\text{Cd}(\text{OH})_2 \cdot s\text{NH}_3 \cdot x\text{H}_2\text{O}$, or in the given case of hydroxy ammoniates, proceeds from dilute aqueous ammonia solutions containing not more than 1.5-2% of ammonia. The region for the existence of the hydroxide precipitates ends at a concentration of about 0.75 wt. % of ammonia in the solutions. The exchange between the ammonium hydroxide and the cadmium chloride increases with increase in ammonia concentration in the limits of the region for deposition of the hydroxide precipitates.

Two compounds crystallize at 0° in the crystallization region for the ammoniates: $\text{CdCl}_2 \cdot 2\text{NH}_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot 6\text{NH}_3 \cdot 1.5\text{H}_2\text{O}$. The compositions of these compounds were determined by the method of residues and by chemical analysis. The experimental results obtained in studying the solubility of the system $\text{CdCl}_2 - \text{NH}_3 - \text{H}_2\text{O}$ at 0° are shown in Fig. 1.

The crystallization of $\text{CdCl}_2 \cdot 2\text{NH}_3 \cdot 1.5\text{H}_2\text{O}$ in the system $\text{CdCl}_2 - \text{NH}_3 - \text{H}_2\text{O}$ at 0° begins with a 0.75-0.80 wt. % and ends with a 21.18 wt. % of ammonia in the equilibrium solution. The point on the diagram for the mutual crystallization of the cadmium di- and hexamine chlorides corresponds to a solution composition of 21.18 wt. % of NH_3 , 37.72 wt. % of CdCl_2 and 41.10% of water.

The solubility of the diammine in aqueous ammonia solutions is directly proportional to the ammonia concentration and is independent of temperature. The solution molar ratio for $\text{NH}_3:\text{CdCl}_2$ in the diammine crystallization region, both at 0° and at 25° , remains constant and ranges in value from 6.25 to 6.40.

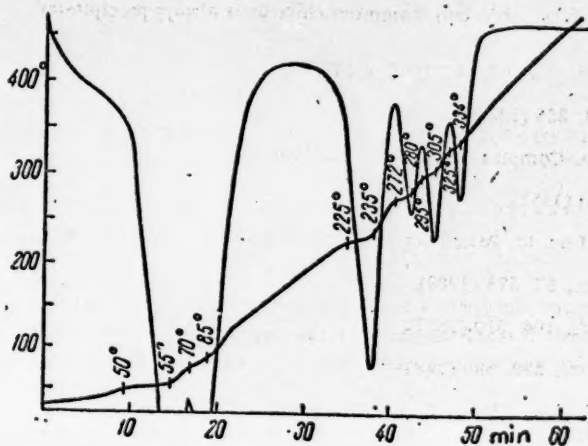


Fig. 3. Heating curves of $\text{CdCl}_2 \cdot 6\text{NH}_3 \cdot 1.5\text{H}_2\text{O}$

The rate of salting out (variation in the solution concentration of the CdCl_2) for $\text{CdCl}_2 \cdot 6\text{NH}_3 \cdot 1.5\text{H}_2\text{O}$ decreases with increase in the solution concentration of the ammonia.

Two compounds also crystallize out at 25° in the system $\text{CdCl}_2 - \text{NH}_3 - \text{H}_2\text{O}$: cadmium monoaquodiammine chloride and $\text{CdCl}_2 \cdot 5.5\text{NH}_3 \cdot 1.5\text{H}_2\text{O}$. Here, the same as at 0° , the CdCl_2 (more correctly, the cadmium diammine chloride) solubility is directly proportional to the ammonia concentration in solution and in its magnitude completely agrees with the solubility values for cadmium chloride at 0° . The results on the solubility of the system $\text{CdCl}_2 - \text{NH}_3 - \text{H}_2\text{O}$ at 25° are shown on the diagram in Fig. 1. As was already indicated, the solubilities of cadmium chloride in aqueous ammonia solutions, in the region of crystallization for cadmium diammine chloride and the higher ammoniates, are completely the same at 0 and at 25° .

The solubility of cadmium chloride in the crystallization region of the higher ammoniates of cadmium chloride depends on the temperature. The variation in the compositions of the compounds crystallizing at 25° can be explained by the stability of the compounds that are formed in the system at different temperatures. Probably the cadmium hexammine chloride is unstable at 25° , and for this reason it cannot crystallize from an aqueous medium at this temperature.

Cadmium diammine chloride is a stable compound, the decomposition of which begins at 223° . The crystallization water in cadmium diammine chloride is removed very rapidly at room temperature, in the course of 15-20 minutes. For this reason the diammine chloride with water of crystallization has not been described up to now. The air-dried diammine fails to contain any water. In contrast to the diammine, the hexammine is an unstable compound; exposure to the air for 1.5-2 hours results in the loss of 4 moles of ammonia and water to give the anhydrous diammine.

The heating curve for the anhydrous cadmium diammine chloride is shown in Fig. 2, where four endothermic heat effects are found to exist. The first effect, beginning at 223° and continuing to 235° , corresponds to the removal of a half mole of ammonia. The second effect at 281° , and also the third at 306° , correspond to the removal of another half mole of ammonia. The fourth effect from 330° to 341° corresponds to the fusion of the cadmium monoammine chloride. Under further heating the monoammine chloride decomposes to the melting point of cadmium chloride and partially sublimes.

On the heating curve for $\text{CdCl}_2 \cdot 6\text{NH}_3 \cdot 1.5\text{H}_2\text{O}$ (see Fig. 3) the endothermic effect at $50-55^\circ$ corresponds to the simultaneous removal of the water of crystallization and two moles of ammonia. At $70-85^\circ$ two moles of ammonia are removed and the diammine remains. The decomposition of this residual portion completely agrees with that of the diammine.

In the above indicated compounds the water, and in the higher ammoniates the ammonia, are extremely labile and they can be "eluted" by different organic solvents (alcohol, ether, etc.).

If ethyl alcohol is added to an ammoniacal cadmium chloride solution, then, independent of the ammonia concentration in solution, the anhydrous cadmium diammine chloride is always precipitated.

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ULTRAVIOLET ABSORPTION SPECTRA OF SOME β -KETO PHOSPHINIC ACID ESTERS

Academician B.A. Arbuzov and V.S. Vinogradova

Extensive literature exists on the ultraviolet absorption spectra of acetoacetic ester and other β -keto acids, and also on β -diketones. The absorption spectra offer valuable information as to the enolization of β -dicarbonyl compounds in different solvents in acid, neutral and alkaline media (see, for example, [1]).

In previous brief communications we gave some data on the synthesis [2] and study by the bromine titration method [3] of a number of β -keto phosphinic acid esters for the purpose of elucidating the presence or absence of keto-enol tautomerism in these phosphorus derivatives. In this communication we give the results of studying their absorption spectra in the ultraviolet region*.

We took the absorption spectra of the phosphonoacetate, the methylphosphonoacetate and the dimethylphosphonoacetate in methyl alcohol and in methyl alcohol containing sodium methylate. The absorption spectra of the phosphonoacetate and dimethylphosphonoacetate are shown in Fig. 1.

The spectra of the three indicated compounds in methyl alcohol are very close and resemble the spectrum of malonic ester, of which they are the phosphorus analogs. The absorption spectra of the phosphonoacetate and methylphosphonoacetate differ but slightly from the spectrum of the dimethylphosphonoacetate, the latter being incapable of enolization, which fact confirmed the bromine titration data, indicating the absence of noticeable amounts of the enol form. The absorption spectra of the phosphonoacetate and the methylphosphonoacetate in sodium methylate solution differ but slightly from those in methyl alcohol, which indicates that in the presence of sodium methylate the enolate ions are formed in small amounts. As was to be expected, the absorption spectra of the dimethylphosphonoacetate in methyl alcohol and in sodium methylate solution were the same.

According to its infrared spectra data [4] diethyl malonate forms enolate ions only to the extent of 30-35%, whereas the esters of β -keto acids in the presence of sodium ethylate give 95-100% of enolate ions.

The data on the absorption spectra of phosphonoacetone and its substituted derivatives proved to be somewhat more complicated.

The spectrum of phosphonoacetone, obtained from triethyl phosphate in methyl alcohol solution, is very close to the spectrum of acetoacetic ester in water, where the enol content is 0.4%, which fact makes probable the low degree of enolization shown by the phosphonoacetone (Fig. 1, B). In sodium methylate solution the phosphonoacetone absorption spectrum gives a maximum in the 2400 Å region, which indicates the presence of a considerable amount of enolate ions. A similar picture was obtained for the ester of β -ketobutylphosphinic acid (Fig. 1, C). The magnitude of the maximum depends on the sodium methylate concentration.

The complete analogy in the change of the absorption spectra for alcohol solutions of the phosphorus analogs of β -dicarbonyl compounds (β -keto acids) when alcoholates are added is also observed for the β -keto sulfones. In Fig. 1, C on the left are given the literature data [5] for the absorption spectra of butyl acetyl sulfone in alcohol and in 0.01N sodium ethylate solution, which data are completely analogous to those obtained by us for the β -ketobutylphosphinic ester (Fig. 1, C, right).

The fact that the solvent fails to appreciably change the absorption spectrum of phosphonoacetone (methyl alcohol, hexane, water) proved to be somewhat unexpected, since for acetoacetic ester the equilibrium changes considerably with solvent (46.4% of the enol in hexane, and 0.4% in water). However, there is some data that

*We wish to thank L.A. Kazitsina for his assistance in the present work.

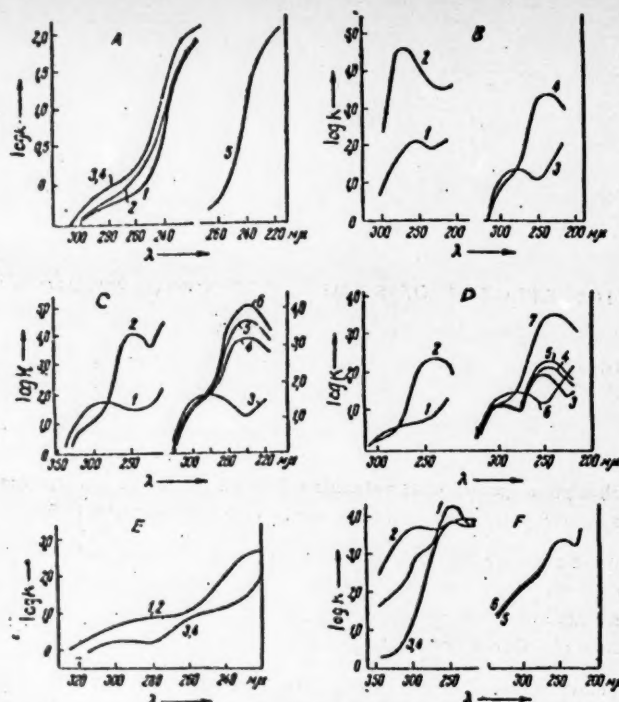


Fig. 1. Absorption Spectra

- A. Phosphonoacetate: 1 - in CH_3OH , 2 - in $\text{CH}_3\text{ONa}^\circ$. Dimethylphosphonoacetate: 3 - in CH_3OH , 4 - in $\text{CH}_3\text{ONa}^\circ$. Malonic ester: 5 - in CH_3OH .
- B. Acetoacetic ester: 1 - in H_2O , 2 - in $\text{C}_2\text{H}_5\text{ONa}$. Phosphonoacetone: 3 - in CH_3OH , $c = 1.3 \cdot 10^{-2}$; 4 - in CH_3ONa , $c = 1.5 \cdot 10^{-2}$, $c_{\text{sub}} = 1.9 \cdot 10^{-2}$.
- C. Butylacetyl sulfone: 1 - in $\text{C}_2\text{H}_5\text{OH}$, 2 - in $\text{C}_2\text{H}_5\text{ONa}$. 8-Ketobutylphosphinic acid ester: 3 - in CH_3OH ; 4 - in $\text{CH}_3\text{ONa}^\circ$; 5 - in CH_3ONa , $c = 5.7 \cdot 10^{-2}$, $c_{\text{sub}} = 2.1 \cdot 10^{-2}$; 6 - in CH_3ONa , $c = 2.2 \cdot 10^{-1}$, $c_{\text{sub}} = 1.2 \cdot 10^{-2}$.
- D. Phosphonoacetone, obtained with sodium diethyl phosphite: 1 - in CH_3OH ; 2 - in $\text{CH}_3\text{ONa}^\circ$, $c = 1.4 \cdot 10^{-2}$, $c_{\text{sub}} = 1.3 \cdot 10^{-2}$; 3 - in CH_3OH ; 4 - in CH_3ONa , $c = 1.6 \cdot 10^{-1}$, $c_{\text{sub}} = 1.6 \cdot 10^{-2}$. Phosphonoacetone, obtained with triethyl phosphite: 5 - in CH_3OH ; 6 - in CH_3ONa ; 7 - in $\text{CH}_3\text{ONa}^\circ$.
- E. Dimethylphosphonoacetone, obtained with sodium diethyl phosphite: 1 - in CH_3OH , 2 - in $\text{CH}_3\text{ONa}^\circ$. Dimethylphosphonoacetone, obtained with triethyl phosphite: 3 - in CH_3OH , 4 - in $\text{CH}_3\text{ONa}^\circ$.
- F. Phosphonoacetophenone, obtained with triethyl phosphite: 1 - in CH_3OH , $c = 8.5 \cdot 10^{-4}$; 2 - in CH_3ONa , $c = 4.4 \cdot 10^{-2}$, $c_{\text{sub}} = 8.6 \cdot 10^{-4}$. Dimethylphosphonoacetophenone: 3 - in CH_3OH , 4 - in $\text{CH}_3\text{ONa}^\circ$. Phosphonoacetophenone, obtained with sodium diethyl phosphite: 5 - in CH_3OH ; 6 - in CH_3ONa , $c = 3.4 \cdot 10^{-2}$, $c_{\text{sub}} = 1.8 \cdot 10^{-2}$.

*The spectra was taken in absolute alcohol, containing 1 mole of sodium alcoholate for 1 mole of substance.

indicates that this influence of the solvent is not always present [6, 7]. Since the unsaturation shown by the phosphonoacetone could be due to contamination by isopropenylethyl phosphate, we took the absorption spectrum of the latter in methyl alcohol and in sodium methylate solution (Fig. 1, D).

As can be seen, the absorption maximum for the phosphate lies in the 2500 Å region, which region corresponds to the minimum for the phosphonoacetone. Sodium methylate raises the absorption in the 2500 Å region, without changing the basic character of the curve.

The absorption spectrum for the phosphonoacetone obtained from bromoacetone and sodium diethyl phosphite differs from the absorption spectrum of the phosphonoacetone obtained from triethyl phosphite and bromoacetone by a smoother character and the absence of a maximum in the 2800 Å region.

In sodium methylate solution, however, in this case also there appears a maximum in the 2400 Å region, characteristic for enolate ions (Fig. 1, D). The dimethylphosphonoacetone, obtained with sodium diethyl phosphite, contained a very small amount of bromine titratable (less than 2%). The absorption curve for this compound had a maximum at 2200, 2300 Å and failed to change when sodium methylate was added (Fig. 1, E).

The phosphonoacetophenone, obtained from triethyl phosphite, gave a coloration with ferric chloride and by bromine titration contained 9% of unsaturates.

The absorption spectrum of phosphonoacetophenone in methyl alcohol almost completely repeats the spectrum of acetophenone, which shows the basic influence exerted by the benzoyl group on the spectrum. A comparison of the phosphonoacetone absorption spectrum with that of the benzoylacetic ester permits making the conclusion that the maximum at 2450 Å belongs to the keto form, and the maximum at 2850 Å to the enol form (Fig. 1, F).

As in the case of the phosphonoacetone, hexane fails to appreciably change the absorption curve for phosphonoacetophenone. In water the absorption decreases in the 2850 Å region, which can indicate a reduction in the amount of the enol form. In the presence of sodium methylate the absorption decreases in the 2450 Å region and strongly increases in the 2800-3100 Å region. For the case of benzoylacetic ester a sharp increase in absorption is produced by sodium ethylate in the 3060 Å region, which increase is attributed to the sodio derivative of the enol form, possessing a clawlike character. As a result, it could be postulated that the absorption increase shown in the 2800-3100 Å region for phosphonoacetophenone is due to the appearance of either enolate ions or of clawlike compounds. A similar picture was also observed for methylacetophenone.

The absorption spectrum for dimethylphosphonoacetophenone, incapable of enolization, shows a sharp absorption increase in the 2450 Å region (keto form) and fails to have a maximum in the 2850 Å region (enol form). The spectra of dimethylphosphonoacetophenone in methyl alcohol and in sodium methylate solution are completely identical.

The presented material shows the analogy that exists between the β -keto and the β -carbalkoxy derivatives of the phosphinic and carboxylic acid esters.

The phosphonoacetic ester, similar to malonic ester, fails to contain much enol.

The phosphonoacetone, probably, contains only a small amount of the enol form. In the case of phosphonoacetophenone the obtained data suggest the presence of the enol form. For all of the enumerated types of compounds in the presence of sodium methylate there occurs either the formation of enolate ions or of clawlike compounds.

However, for the organophosphorus compounds, containing a phosphono group and a carbonyl group in the β -position, the picture is considerably more complicated than it is for carbon compounds and further studies are needed to answer some of the obscure questions that arose in our study of this interesting field of organic phosphorus derivatives.

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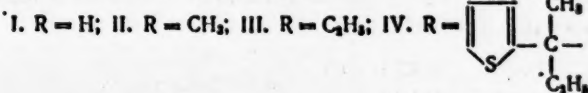
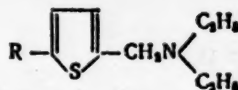
SYNTHESIS OF ALIPHATIC TERTIARY AMINES FROM THIOPHENE DERIVATIVES

Ya. L. Goldfarb and M.B. Ibragimova

(Presented by Academician A.A. Balandin, July 28, 1955)

As is known, the aliphatic or aliphatic-aromatic tertiary amines and, especially, the quaternary ammonium salts formed by them, possess well defined physiological activity, as for example, hypotensive or anticholinesterase action. In connection with this it is of interest to develop a convenient method for the synthesis of such amines, which method would permit varying both the length of the chain and the degree of branching of the radicals attached to the nitrogen. As it seems to us, some of these characteristics are inherent in the method described below, which method is based on the hydrogenolysis of the corresponding thiophene compounds; this method is illustrated by several examples.

The starting amines, and specifically, diethyl-2-thenylamine (I), diethyl(5-methyl-2-thenyl)amine (II), diethyl(5-ethyl-2-thenyl)-amine (III) and 2,2-[2'-thienyl-(5-diethylaminomethyl)-2-thienyl]-butane (IV) were obtained by the Leuckart reaction, which with respect to (I) was described by Smith and Cavallito [1].



In general, the yields of these amines corresponded to those given in the above-mentioned work, and failed to exceed 67%. These amines under hydrogenolysis with Raney nickel by the usual method, which method was studied many times in our laboratory [2,3], gave, respectively, diethylamylamine (V), diethylhexylamine (VI), diethylheptylamine (VII) and diethyl(6-methyl-6-ethyldecyl)amine (VIII), which were characterized as such or as their salts. The yield in the hydrogenolysis step varied from 46 to 66%, possibly due to the fact that part of the amine was deaminated under the influence of Ni.

It is quite evident that the method of introducing various substituents into the thiophene nucleus, both in the α - and in the β -positions, makes it possible to synthesize various amines of the thiophene series by the above-mentioned method, the hydrogenolysis of which permits obtaining various aliphatic tertiary amines of both normal and iso structure.

EXPERIMENTAL

The above-mentioned tertiary amines of the thiophene series were prepared by the Smith and Macdonald method [4], modified by Smith and Cavallito [1], which consisted in heating a mixture of the proper aldehyde, diethylamine and 96% formic acid for 10 hours. After suitable treatment [4] the base was vacuum-distilled, while the unchanged aldehyde was recovered from the hydrochloric acid solution.

In this way from 56 g (0.5 mole) of thiophenealdehyde, 60 g (1.25 mole) of formic acid and 78 g (1 mole)

of diethylamine we obtained 56.31 g (67% of the theoretical) of (I); b.p. 98-100° (18 mm); n_D^{20} 1.5092. Smith and Cavallito [1] show b.p. 40° (1.5 mm) and n_D^{20} 1.5095.

Heating for a short time of a mixture of 0.5 g of the amine (I) with 0.5 ml of methyl iodide gave the corresponding methiodide. After 3 recrystallizations from absolute alcohol, m.p. 151.5-152°. According to Smith and Cavallito [1], diethylmethyl-2-thenylammonium iodide melts at 156°.

Found %: N 4.46; 4.43
 $C_{10}H_{13}NSI$. Calculated %: N 4.50

Diethyl(5-methyl-2-thenyl)amine (II). From 12.6 g (0.1 mole) of 5-methyl-2-thiophenealdehyde, 12 g (0.25 mole) of formic acid and 14.6 g (0.2 mole) of diethylamine there was obtained 10 g (54.7% of the theoretical calculated from the equation) of the amine with b.p. 94.5-95° (8.5 mm) and n_D^{20} 1.5069.

Found %: N 7.51; 7.77
 $C_{10}H_{11}NS$. Calculated %: N 7.64

The (II) methiodide was obtained in the same manner as the methiodide of (I); after two recrystallizations from absolute alcohol it melted at 125.5-126°.

Found %: N 4.23; 4.42
 $C_{11}H_{13}NSI$. Calculated %: N 4.31

Diethyl(5-ethyl-2-thenyl)amine (III). From 14 g (0.1 mole) of 5-ethyl-2-thiophenealdehyde, 12 g (0.25 mole) of formic acid and 14.6 g (0.2 mole) of diethylamine there was obtained 10.85 g (50% of the amount calculated from the equation) of amine with b.p. 109° (8-9 mm); n_D^{20} 1.5050; d_4^{20} 0.9568; MR_D calculated 61.87, found 61.16.

Found %: N 7.09; 7.19
 $C_{11}H_{13}NS$. Calculated %: N 7.10

The picrate of this amine was obtained by mixing ether solutions of (III) and picric acid. After recrystallization from aqueous alcohol it melted at 91.5-92.5°.

Found %: N 13.12; 13.31
 $C_{17}H_{21}N_4O_7S$. Calculated %: N 13.14

2,2-[2'-Thienyl-(5-diethylaminomethyl)-2-thienyl]butane (IV). From 7.3 g (0.03 mole) of 2,2-[2'-thienyl-(5-formyl)-2-thienyl]-butane, 4.37 g (0.06 mole) of diethylamine and 3.45 g (0.075 mole) of formic acid there was obtained 4.3 g (50% of the calculated amount) of amine with b.p. 151-152° (3 mm) and n_D^{20} 1.5538.

Found %: N 4.61; 4.80
 $C_{17}H_{23}NS_2$. Calculated %: N 4.56

The oxalate was obtained by mixing ether solutions of the amine (IV) and anhydrous oxalic acid; after 4-fold reprecipitation from alcohol with ether the m.p. was 77.5-78.5°.

Found %: N 3.65
 $C_{19}H_{27}NS_2O_4$. Calculated %: N 3.53

The hydrogenolysis of the above-mentioned amines was run by the method of heating the amine with a 7-fold amount of skeletal Ni-catalyst, prepared by the Adkins method [5]. The amine was placed in a flask, fitted with stirrer and a reflux condenser connected to a calcium chloride tube, together with a 3-fold amount of absolute alcohol. Then to this in small portions with the aid of absolute benzene (20 parts of benzene for 3 parts of alcohol taken for reaction) was added the catalyst, previously washed with alcohol to remove traces of moisture. The mixture was then boiled with vigorous stirring until the test for sulfur was negative. The catalyst was transferred to a Soxhlet apparatus and the reaction mixture was extracted, after which the solvent was distilled from a flask fitted with a Vigreux column at 65-75°.

Diethylamylamine (V). The heating of 7 g of amine (I) with Raney nickel for 1.5 hours gave 3.2 g (54% yield) of an amine with b.p. 155-158°; n_D^{20} 1.4193; d_4^{20} 0.7702; MR_D calculated 47.70; found 47.01. Redistillation gave the following fractions:

1. 120-155° - 0.35 g; n_D^{20} 1.4170.
2. 155-157° - 1.2 g; n_D^{20} 1.4197.
3. 157-158° - 0.15 g; n_D^{20} 1.4202.

According to Prevost [6] the b.p. of diethylamylamine is 155°.

Analysis of the second fraction:

Found %: C 75.54; 75.35; H 14.51; 14.36; N 9.76; 9.71
C₉H₂₁N. Calculated %: C 75.45; H 14.78; N 9.78

Diethylhexylamine (VI). The heating of 6 g of amine (II) with Raney nickel for 1 hour and 20 minutes gave 2.3 g (45.7% yield) of an amine with b.p. 175-179°. Redistillation gave:

1. 175-179° - 0.65 g; n_D^{20} 1.4245
2. 179-180° - 1.42 g; n_D^{20} 1.4245

Analysis of the second fraction:

Found %: C 76.07; 76.25; H 14.35; 14.20; N 8.93; 9.03
C₁₀H₂₃N. Calculated %: C 76.35; H 14.73; N 8.91

The oxalate of (VI) was obtained in the same manner as the oxalate of (IV); after 4-fold reprecipitation from alcohol with ether the m.p. was 76.5-77.5°.

Found %: N 5.59; 5.78
C₁₂H₂₅NO₄. Calculated %: N 5.66

Diethylheptylamine (VII). The heating of 10 g of amine (III) with Raney nickel for 1 hour and 20 minutes gave 4.7 g (53.7% yield) of an amine with b.p. 188-200°. Redistillation gave:

1. 188-198° - 2.26 g; n_D^{20} 1.4282.
2. 198-200° - 2.4 g; n_D^{20} 1.4289.

According to Mannich and Davidsen [7] the diethylheptylamine boils at 198°; Marszak and coworkers [8] give b.p. 86° (14 mm) and n_D^{21} 1.4317.

Analysis of the second fraction:

Found %: C 76.80; 76.93; H 14.73; 14.55; N 8.02; 8.18
C₁₇H₃₅N. Calculated %: C 77.13; H 14.71; N 8.18

The oxalate of (VII) was obtained the same as the oxalate of (IV); after 3-fold reprecipitation from alcohol with ether it melted at 84.7-85.7°. According to Marszak [8] the m.p. of diethylheptylamine oxalate is 80°.

Found %: N 5.67; 5.53
C₁₉H₄₁NO₄. Calculated %: N 5.54

Diethyl(6-methyl-6-ethyldecyl)amine (VIII). The heating of 3.64 g of amine (IV) with Raney nickel for 1 hour and 20 minutes gave 2 g of an amine (66% of the calculated amount) with b.p. 107-167° (18 mm). Redistillation gave:

1. 97-155°/18 mm - 0.77 g; n_D^{20} 1.4380.
2. 159-162°/18 mm - 0.86 g; n_D^{20} 1.4473.

Analysis of the second fraction:

Found %: C 79.91; 79.78; H 14.66; 14.54
C₁₇H₃₇N. Calculated %: C 79.91; H 14.60

The oxalate of (VIII) was obtained the same as the oxalate of (IV); after 3-fold reprecipitation from alcohol with ether it melted at 111-112°.

Found %: N 4.15; 4.13
C₁₉H₃₉NO₄. Calculated %: N 4.05

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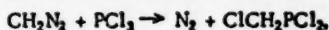
THE IMIDES OF ALKYLPHOSPHORIC ACIDS. TRIALKYLPHOSPHATOAZINES

Acad. Sci. USSR Corresponding Member M.I. Kabachnik and V.A. Gilyarov

Staudinger and Meyer [1] described the reaction of triarylphosphines and trialkylphosphines with aliphatic diazo compounds, as a result of which the so-called phosphazines are formed:

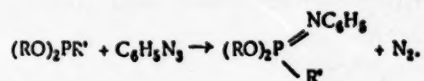


An attempt made by them to extend this reaction to phosphorus trichloride proved unsuccessful. V. Plets [2] noted the formation of tarry products in the reaction of diazomethane with phosphorus trichloride, but A. Ya. Yakubovich and V.A. Ginzburg [3] showed that under certain conditions this reaction proceeds smoothly with formation of the chloromethyldichlorophosphine:

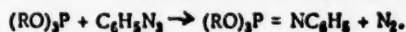


i.e. not by the addition type of reaction at the undivided electron pair of the phosphorus, but by the usual type for elemental chlorides — the formation of chloromethylelement chlorides.

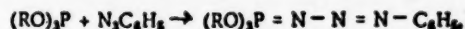
Recently, in studying the tautomerism and reactivity of the dialkylanilidophosphites, we established that the esters of trivalent phosphorus acids react with phenylazide with the evolution of nitrogen and the formation of imidophosphates [4]:



We also showed that the trialkylphosphites easily enter into this reaction with the formation of trialkyl-N-phenylimidophosphates:



Based on the work of Homer and Gross [5] it might be thought that the first step of the reaction is the formation of the triazine:



which, losing a mole of nitrogen, is converted into the corresponding phenylimidophosphate. In such case it might be thought that the aliphatic diazo compounds, in their reactions showing a great similarity to the azides, should also add to the esters of trivalent phosphorus acids, in the first phase to the trialkylphosphites, with the formation of the corresponding phosphatoazines:



We studied this reaction and found that the trialkylphosphites react smoothly with diazomethane to form N-methylenetrialkylphosphatoazines.

The latter are colorless liquids, soluble in organic solvents and insoluble in water. Only the triethyl derivative is somewhat soluble in water. The constants of the obtained substances are given in Table 1.

At the base of the reaction of trialkylphosphites with diazomethane lies the easy addition at the undivided electron pair of the phosphorus with conversion of the trivalent phosphorus compound into the pentavalent phosphorus compound. Consequently, this reaction can be regarded as belonging to the group of reactions that are characteristic for trivalent phosphorus compounds, such as the reaction with sulfur, with cuprous salts, with alkyl halides [6,7], with phenylazide and with the sodium salts of the chloroamides of arylsulfonic acids [8]. To prove the structure of

the *N*-methylenetrialkylphosphatoazines we used the reaction with carbon disulfide. From the studies of Staudinger and coworkers it is known that substances with a P=N bond react with carbon disulfide and are converted into the corresponding thio compounds [9]:

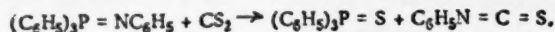
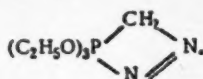


TABLE 1

Substance	B. p., °C	P, mm	n_D^{20}	d_4^{20}	Yield in %
$(\text{C}_2\text{H}_5\text{O})_3\text{P}=\text{N}-\text{N}=\text{CH}_2$	55-57	1	1.4498	1.0664	48
$(\text{C}_3\text{H}_7\text{O})_3\text{P}=\text{N}-\text{N}=\text{CH}_2$	74.5-76	1	1.4485	1.0045	53
$(i\text{-C}_3\text{H}_7\text{O})_3\text{P}=\text{N}-\text{N}=\text{CH}_2$	55	1	1.4440	0.9807	34.6
$(\text{C}_4\text{H}_9\text{O})_3\text{P}=\text{N}-\text{N}=\text{CH}_2$	101-102	1	1.4484	0.9743	42
$(i\text{-C}_4\text{H}_9\text{O})_3\text{P}=\text{N}-\text{N}=\text{CH}_2$	95	1.5	1.4420	0.9675	57

However, in the reaction of phosphazines with carbon disulfide Staudinger and Braunholtz were unable to isolate the products [10].

We found that *N*-methylenetriethylphosphatoazine with carbon disulfide forms triethyl thiophosphate, which we were able to isolate and the constants of which coincided with the literature data [11]. Thus, in one step this reaction demonstrates for *N*-methylenetriethylphosphatoazine the structure $(\text{C}_2\text{H}_5\text{O})_3\text{P}=\text{N}-\text{N}=\text{CH}_2$ and causes rejection of the second proposed structure:



EXPERIMENTAL

***N*-Methylenetrialkylphosphatoazines.** An ether solution of diazomethane was added to an ether solution of the trialkyl phosphite. On standing for several days the yellow color of the diazomethane disappeared, after which the ether was distilled *in vacuo*, and the residue was distilled.

N-Methylenetriethylphosphatoazine was obtained from 8.3 g (0.05 mole) of triethyl phosphite in 15 ml of absolute ether and 120 ml of an ethereal diazomethane solution, containing 0.05-0.07 mole of diazomethane. After two distillations there was isolated 4.8 g of *N*-methylenetriethylphosphatoazine. M_R found 52.47, calculated 52.84.*

Found %: C 40.25; 40.34; H 8.16; 8.20; P 14.94; 15.08; N 12.88; 12.99
 $\text{C}_7\text{H}_{17}\text{O}_3\text{N}_2\text{P}$. Calculated %: C 40.38; H 8.17; P 14.90; N 13.46

N-Methylenetripropylphosphatoazine was obtained from 5.8 g (0.028 mole) of tripropyl phosphite in 15 ml of ether and 80 ml of an ethereal diazomethane solution, containing 0.045-0.055 mole of diazomethane. The yield of *N*-methylenetripropylphosphatoazine was 3.7 g. M_R found 66.77, calculated 66.70.

Found %: C 47.79; 47.62; H 9.34; 9.22; P 12.66; 12.45
 $\text{C}_{10}\text{H}_{23}\text{O}_3\text{N}_2\text{P}$. Calculated %: C 47.94; H 9.19; P 12.39

N-Methylenetrisopropylphosphatoazine was obtained from 6.2 g (0.03 mole) of trisopropyl phosphite in 15 ml of ether and 60 ml of an ethereal diazomethane solution, containing 0.03-0.04 mole of diazomethane. After two distillations there was obtained 2.6 g of *N*-methylenetrisopropylphosphatoazine. M_R found 67.79, calculated 66.70.

Found %: C 48.21; 48.17; H 9.21; 9.36; P 12.06; 12.32
 $\text{C}_{10}\text{H}_{23}\text{O}_3\text{N}_2\text{P}$. Calculated %: C 47.94; H 9.19; P 12.39

N-Methylenetributylphosphatoazine was obtained from 5.0 g (0.02 mole) of tributyl phosphite in 15 ml of ether and 50 ml of an ethereal diazomethane solution, containing 0.03-0.04 mole of diazomethane. Yield 2.5 g. M_R found 80.39; calculated 80.55.

* The atomic refraction of two nitrogen atoms was taken as equal to 8.54 (calculated from the data of the present work).

Found %: C 52.88; 52.91; H 10.02; 10.03; P 10.71; 10.94
 $C_{13}H_{29}O_3N_2P$. Calculated %: C 53.36; H 9.92; P 10.62

N-Methylenetriisobutylphosphatozine was obtained from 7.5 g (0.03 mole) of triisobutyl phosphite in 15 ml of ether and 100 ml of an ethereal diazomethane solution, containing 0.05-0.06 mole of diazomethane. Yield 5.0 g. MR_D found 79.95, calculated 80.55.

Found %: C 52.74; 52.91; H 9.90; 9.98; P 9.80 9.88
 $C_{13}H_{29}O_3N_2P$. Calculated %: C 53.36; H 9.92; P 10.62

Action of Carbon Disulfide on N-Methylenetriethylphosphatozine. Without solvent the reaction of N-methylenetriethylphosphatozine with carbon disulfide is exceedingly violent. To a solution of 3.4 g (0.016 mole) of N-methylenetriethylphosphatozine in 10 ml of dry benzene the carbon disulfide (7.5 g; 0.1 mole) was added dropwise and with ice-cooling. The mixture was heated for 3 hours at 65-70°. Then the carbon disulfide and benzene were removed by vacuum-distillation. Distillation of the residue gave 1.4 g of a liquid with b.p. 73-74° at 5 mm; n_D^{20} 1.4480. The residue after distillation was a dark-brown liquid and weighed 2.6 g. A second distillation gave 1.0 g of triethyl thiophosphate with b.p. 83° at 7 mm; n_D^{20} 1.4440; d_4^{20} 1.0723; d_4^{20} 1.0719. For $C_6H_{15}O_3PS$ MR_D found 49.12, calculated 49.39. Literature for triethyl thiophosphate [11]: b.p. 88.5° at 8 mm; n_D^{20} 1.4480; d_4^{20} 1.0756. With mercuric iodide the triethyl thiophosphate gave a complex of composition $(C_2H_5O)_3P = S \cdot 2HgI_2$; m.p. 101-102°. Its mixed melting point with the complex of known structure was 100-101° (from alcohol). Literature for the complex $(C_2H_5O)_3P = S \cdot 2HgI_2$; m.p. 88° [12].

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*T.p. = C.B. Translation pagination.

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TERNARY AND MORE COMPLEX SOLID SOLUTIONS OF INTERMETALLIC COMPOUNDS

I. I. Kornilov

(Presented by Academician I. P. Bardin, July 23, 1955)

Intermetallic compounds, retaining metallic properties, differ from the metals composing them in their individual properties. On composition-property diagrams they are expressed by singular and special points [1].

Intermetallic compounds, the same as metals, are capable of forming solid solutions. The latter are formed both as the result of mutual solution of intermetallic compounds and as the result of metals dissolving in these compounds in the solid state.

The general situation as to the formation of continuous solid solutions between intermetallic compounds was presented in one of our studies [2]. It was mentioned that the necessary conditions for the formation of these solid solutions are: a one-type crystal lattice for the compounds, the same type of chemical bonding, and atomic affinity between the elements participating in the formation of the compounds.

Proceeding from these postulations the possibility was predicted of forming continuous solid solutions in a number of binary systems, composed of intermetallic compounds. Recently these predictions found experimental confirmation in both our studies [3,4] and in the studies of other authors [5-8]. Thus, for example, the formation of continuous solid solutions was demonstrated in the system composed of the "Kurnakov compounds" • FeCr-FeV [4], in the systems $Ni_3Nb - Ni_3Ta$ [3], $Mo_5Si - W_5Si$ [8], $InAs - InSb$ [7], $Bi_2S_3 - Sb_2S_3$ [9], etc. The last two systems belong to the semiconductor type of compounds.

As a result, there exist many analogous intermetallic compounds, capable, when the above presented conditions are satisfied, of forming solid solutions between themselves.

The above presented conditions are also valid for the formation of ternary and more complex solid solutions of intermetallic compounds, thus determining the possibility for the formation of continuous binary solid solutions of metals. Proceeding from these postulations we can establish a base for the possibility of forming solid solutions between intermetallic compounds in ternary and more complex systems (in accord with the general teaching on equilibrium in binary, ternary and more complex systems [1]).

Without going into a detailed description of the problem of forming ternary and more complex solid solutions of intermetallic compounds, we will present some concrete examples of ternary systems of intermetallic compounds, showing the possibility for the formation of solid solutions.

Below we present some ternary systems of intermetallic compounds, which compounds should form continuous solid solutions. Included in this number of compounds are the Kurnakov compounds, aluminides (compounds with aluminum), titanides, niobides, tantalides, borides, silicides and carbides. The systems of other

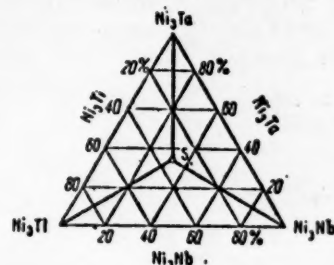


Fig. 1.

*We assign the name of Kurnakov compounds to those compounds that are formed from solid solutions [4].

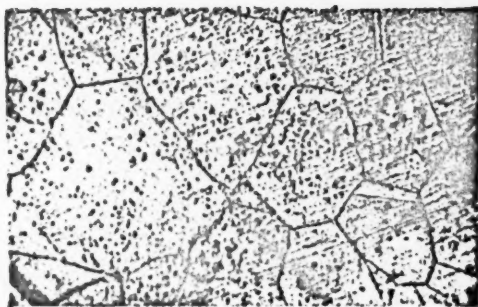


Fig. 2.

compounds can also be classified as belonging here, and namely the arsenides, sulfides and selenides, being compounds of the semiconductor type.

Kumakov Compounds: $\text{Ni}_3\text{Fe} - \text{Ni}_3\text{Cr} - \text{Ni}_3\text{Mn}$; $\text{Fe}_3\text{Cr} - \text{Fe}_3\text{V} - \text{Fe}_3\text{Mo}$; $\text{FeCr} - \text{FeV} - \text{CrCo}$; $\text{FeCo} - \text{FeIr}$ - FePt ; $\text{CuAu} - \text{CuPd} - \text{CuPt}$, etc.

Aluminides: $\text{Fe}_3\text{Al} - \text{Ni}_3\text{Al} - \text{Co}_3\text{Al}$; $\text{FeAl} - \text{NiAl} - \text{CoAl}$, etc.

Titanides, Niobides and Tantalides: $\text{Ni}_3\text{Ti} - \text{Ni}_3\text{Nb} - \text{Ni}_3\text{Ta}$; $\text{Ni}_3\text{Ti} - \text{Co}_3\text{Ti} - \text{Ni}_3\text{Nb}$; $\text{Ni}_3\text{Ti} - \text{Co}_3\text{Ti} - \text{Ni}_3\text{Ta}$, etc.

Borides: $\text{TiB}_2 - \text{ZrB}_2 - \text{HfB}_2$; $\text{TiB}_2 - \text{VB}_2 - \text{CrB}_2$; $\text{TiB}_2 - \text{VB}_2 - \text{NbB}_2$; $\text{VB}_2 - \text{NbB}_2 - \text{TaB}_2$; $\text{NbB}_2 - \text{MoB}_2 - \text{TaB}_2$, etc.

Silicides: $\text{TiSi}_2 - \text{VSi}_2 - \text{MoSi}_2$; $\text{TiSi}_2 - \text{VSi}_2 - \text{CrSi}_2$; $\text{CrSi}_2 - \text{MoSi}_2 - \text{WSi}_2$; $\text{V}_3\text{Si} - \text{Cr}_3\text{Si} - \text{Mo}_3\text{Si}$ [10], etc.

Carbides: $\text{TiC} - \text{ZrC} - \text{HfC}$; $\text{TiC} - \text{NbC} - \text{TaC}$; $\text{VC} - \text{NbC} - \text{TaC}$, etc.

Similar systems have not yet been experimentally studied; even many of the intermetallic compound binary systems, composing these ternary systems, still remain unstudied. In the order of preliminary examination of this problem and to prove the possibility of forming ternary solid solutions of intermetallic compounds, we took as our first subject for study the ternary system of compounds $\text{Ni}_3\text{Ti} - \text{Ni}_3\text{Nb} - \text{Ni}_3\text{Ta}$. Proceeding from theoretical [2], and in part experimentally demonstrated by us [3], considerations as to the formation of continuous solid solutions in the corresponding binary systems of these compounds, we prepared a melt of the three compounds with but a single composition, which composition corresponded to point S on the concentration triangle of the ternary system $\text{Ni}_3\text{Ti} - \text{Ni}_3\text{Nb} - \text{Ni}_3\text{Ta}$ (see Fig. 1). After prolonged homogenizing annealing (at 1250° for 100 hours) of the alloy this composition showed a uniform structure (see Fig. 2). An x-ray study of this ternary alloy of intermetallic compounds revealed a like system of lines, corresponding to the hexagonal lattice. As a result, the presence of continuous solid solutions in the ternary system of the intermetallic compounds $\text{Ni}_3\text{Ti} - \text{Ni}_3\text{Nb} - \text{Ni}_3\text{Ta}$ was demonstrated by the microscopic and x-ray analysis data obtained for a single composition of the ternary alloy of these compounds. By analogy, it can be assumed that it is also possible to form many other ternary solid solutions of intermetallic compounds, composed of borides, silicides, carbides, etc.

Reasoning further, it can also be postulated that solid solutions of intermetallic compounds, more complex than the ternary alloys, are capable of existence, either as continuous solutions or within certain concentration limits.

The formation of continuous quaternary solid solutions is possible for: $\text{TiB}_2 - \text{VB}_2 - \text{NbB}_2 - \text{TaB}_2$; $\text{TiSi}_2 - \text{VSi}_2 - \text{NbSi}_2 - \text{MoSi}_2$; $\text{VC} - \text{NbC} - \text{TiC} - \text{MoC}$, etc., and of limited quaternary solid solutions for the compounds: $\text{Ni}_3\text{Ti} - \text{Ni}_3\text{Nb} - \text{Ni}_3\text{Ta} - \text{Ni}_3\text{Al}$; $\text{Ni}_3\text{Ti} - \text{Co}_3\text{Ti} - \text{Ni}_3\text{Ta} - \text{Ni}_3\text{Al}$; $\text{TiB}_2 - \text{ZrB}_2 - \text{HfB}_2 - \text{MoSi}_2$, etc.

In their properties such intermetallic compound solid solutions differ sharply from the properties of metal solid solutions. In order to emphasize this difference, the intermetallic compound solid solutions should be called molecular solid solutions [2], formed by metal compounds.

As a result, a wide variety of a new class of complex inorganic substances is uncovered, corresponding to the solid solutions of intermetallic compounds, a systematic study of whose structure and properties we have just started.

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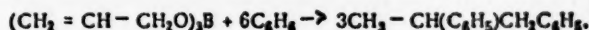
ALKYLATION OF AROMATIC HYDROCARBONS WITH BORIC ACID ESTERS

V.K. Kuskov and B.M. Sheiman

(Presented by Academician S.I. Volfovich, July 27, 1955)

Usually, alkyl halides, alkenes [1], or alcohols are used in Friedel-Crafts alkylations of aromatic hydrocarbons. In the latter instance, more than a molecular amount of aluminum chloride is required, and the yield is often low. Alkylation of benzene with butyl alcohol was accomplished by P.I. Tsukervanik and Kh. Taveeva [3] in an improved manner in a continuous flow apparatus; the aluminum chloride consumption was 1.2 moles per mole of alcohol, and the yield of sec-butylbenzene was 34%. By the condensation of allyl alcohol with benzene in the presence of aluminum chloride, Huston [4] obtained allylbenzene in 16% yield and 1,2-diphenylpropane in 2% yield. Condensation of allyl alcohol with benzene in the presence of sulfuric acid gave 1,2-diphenylpropane in 32% yield and much resinous material. Alkylation with esters has found limited use (e.g., methylation of benzene with dimethyl sulfate [5]), chiefly because they have no advantages over alcohols. We have found that boric acid esters are relatively convenient alkylating agents. With these agents, the alkylation reaction proceeds at somewhat milder conditions than with alcohols. Upon alkylation of benzene with tributyl borate, we obtained sec-butylbenzene in good yield (78%), and, analogously, from isobutyl borate and benzene we obtained tert-butylbenzene. It is noteworthy that, notwithstanding the indications of B.V. Tronov and A.M. Petrova [6], we obtained no organo-boron compounds. During the alkylation, the aluminum chloride consumption did not exceed 1.5 moles per mole of trialkyl borate, that is, 0.5 mole per equivalent.

It was shown that double alkylation of aromatic hydrocarbons with borate esters of unsaturated alcohols or halohydrins is quite possible. By the interaction of triallyl borate with benzene, we obtained 1,2-diphenylpropane with a yield of 46% of theory:



The best aluminum chloride consumption was 1.5 moles per mole of triallyl borate, that is, 0.5 equivalents. Isopropylbenzene was a by-product. The 1,2-diphenylpropane was identical with that prepared earlier by M. Kononov and S. Dobrovolsky [7]. Analogously, 1,2-ditolylpropane, prepared previously by S. Zhukovsky [8] by the action of zinc on a mixture of allyl bromide and toluene, was obtained with an overall yield of 4%. By the reaction of ethylene chlorohydrin borate with benzene, toluene, and *m*-xylene, we obtained, respectively, 1,2-diphenyl-, 1,2-ditolyl-, and 1,2-di(*m*-xylyl)ethane in good yields. An attempt to substitute iron chloride for aluminum chloride in this synthesis gave negative results.

Condensation of ethylene chlorohydrin directly with benzene gives dibenzyl [9] with a total yield of 39% and with a large consumption of aluminum chloride. Borate esters are easily prepared by the reaction of alcohols with boric acid with the elimination of water. Thus, borate esters are more convenient than others for Friedel-Crafts alkylation, particularly since aluminum chloride consumption is less than in alkylations with other esters or with alcohols.

EXPERIMENTAL

Synthesis of borate esters. Triallyl borate was prepared in a Dean and Stark apparatus with a water separator tube by boiling 114 g (2 moles) of allyl alcohol, 31 g (0.5 mole) of boric acid, and 175 ml of benzene until distillation of the water-allyl alcohol azeotrope ceased, practically 8 hours. The benzene and excess allyl alcohol were distilled off, the triallyl borate was fractionated, and the fraction boiling at 175-177° (741 mm)

was collected. By a second fractionation of the first fraction, which was a mixture of allyl alcohol and tri-allyl borate, 18.5 g of triallyl borate was obtained for an overall yield of 84 g (92% of theoretical), d_4^{20} 0.9215; n_D^{20} 1.4285.

Found % B 5.89

$C_9H_{15}O_3B$. Calculated %: B 5.94

Tri- β -chloroethyl borate was obtained in a similar manner using 1 mole of boric acid, 3 moles of ethylene chlorohydrin, and 75 ml of benzene. The reaction time was 5 hours. The product was distilled in a vacuum, b.p. 121-123° (6 mm). The yield was 236 g (94% of theoretical).

Tributyl borate and triisobutyl borate were prepared analogously by boiling 1 mole of boric acid with 4 moles of butyl alcohol until the water was completely eliminated. The yields were 95.6 and 93% of theory, respectively.

Condensation of tributyl borate with benzene. The experiments were carried out in a three-neck, round bottom flask provided with a stirrer, a reflux condenser, and a thermometer. To 15 g (0.066 mole) of tributyl borate and 120 ml (1.35 moles) of dry benzene was added 13.3 g (0.1 mole) of aluminum chloride over the course of an hour. The mixture was then warmed for 1 hour at 50-60° and for 5 hours on a boiling water bath. After the usual treatment (hydrolysis, separation, drying, and distillation with a spiral deflegmator of 10-mm height), there was obtained 20.5 g of a fraction boiling at 140-200°, butylbenzene (78% of theory), and 1.45 g of a fraction boiling at 200-240°, dibutylbenzene (3.9% of theory). A second fractionation produced 17.7 g of *sec*-butylbenzene: b.p. 171.5-172.5° (744 mm); d_4^{20} 0.8598; n_D^{20} 1.4900; $MR_D = 45.08$ (calculated 44.78), which properties are in agreement with literature data [10, 11]. Benzoic acid was obtained upon oxidation of the material.

Analogously, from 15 g (0.066 mole) of triisobutyl borate, 225 ml (2.5 moles) of benzene, and 11.9 g (0.088 mole) of aluminum chloride warmed for 5 hours at 45 to 70°, there was obtained 14.4 g (55%) of *tert*-butylbenzene, b.p. 140-200°; after a second fractionation, the fraction boiling at 168-170° (744 mm) had these properties: d_4^{20} 0.8612; n_D^{20} 1.4908; $MR_D = 45.043$, which properties are in agreement with literature data [10, 11]. 2.1 g of a fraction boiling at 200-240° were obtained (11.2% of theory calculated as dibutylbenzene).

Condensation of triallyl borate. To 9.1 g (0.05 mole) of triallyl borate and 180 ml (2 moles) of benzene was added 10.2 g (0.075 mole) of aluminum chloride over the course of 3 hours. The mixture was warmed 12 hours at 60-65° and then 1 hour at 75°. The end of the reaction was determined by the disappearance of the double bonds (reaction with bromine water). There was obtained 13.6 g (46%) of 1,2-diphenylpropane boiling at 148-150° (15 mm) and 281-283° (752 mm); d_4^{20} 0.9810; n_D^{20} 1.5595; $MR_D = 64.54$ (calculated 64.27), which properties agree with the literature data [7]. There was also obtained some isopropylbenzene; b.p. 155-156°; d_4^{20} 0.8640; n_D^{20} 1.4937; $MR_D = 40.41$ (calculated 40.16).

Analogously, from toluene, warmed 9 hours at 45-55°, there was obtained 19.5 g (58%) of 1,2-ditolylpropane; b.p. 138-140° (3 mm) and 308-309° (741 mm); d_4^{20} 0.9658; n_D^{20} 1.5509; $MR_D = 73.985$ (calculated 73.504), which properties are in agreement with the literature data [8]. Oxidation yielded a mixture of isophthalic and terephthalic acids, the first being obtained in the larger amounts.

Condensation of tri- β -chloroethyl borate. To 5 g (0.02 mole) of tri- β -chloroethyl borate and 85 ml (0.8 mole) of dry benzene was added 8 g (0.06 mole) of aluminum chloride over the course of 1 hour, and the mixture was warmed 12 hours at 75°. 9 g (82%) of dibenzyl was obtained; m.p. (crystallized from alcohol) 51-52°; b.p. 281-283° (735 mm), which properties are in agreement with the literature data [10].

Analogously, from toluene was obtained 9.8 g (77%) of ditolyethane; b.p. 163-164° (10 mm); d_4^{20} 0.9684; n_D^{20} 1.5570. Literature data for symmetrical di-*m*-tolylethane: b.p. 163° (10 mm); d_4^{20} 0.9743; n_D^{20} 1.5568 [12]. Oxidation gave a mixture of isophthalic and terephthalic acids with the former predominating.

From *m*-xylene was obtained 11.6 g (81%) of 1,2-dixylyethane; b.p. 142-143° (3 mm); d_4^{20} 0.9709; n_D^{20} 1.5555; $MR_D = 78.741$ (calculated 78.122).

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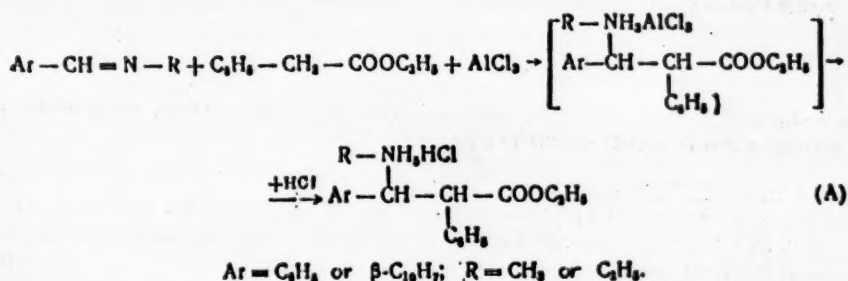
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SYNTHESIS OF ESTERS OF α -PHENYL- β -ARYL- β -ALKYLAMINOPROPIONIC ACIDS FROM ARYLIDENALKYLAMINES AND ETHYLPHENYL ACETATE IN THE PRESENCE OF ANHYDROUS ALUMINUM CHLORIDE

N.M. Mollov

(Presented by Academician I.N. Nazarov, September 26, 1955)

In previous communications by the author and B.I. Kurtev, it was shown that, in the presence of anhydrous aluminum chloride, ethylphenyl acetate can add to the carbon-nitrogen double bond of arylidenanils [1] and hydramides [2] to give the esters of β -anilino- and β -amino- α -phenyl- β -arylpropionic acids, respectively. In the present work, this reaction is extended to Schiff bases prepared from aromatic aldehydes and alkyl amines. In this case, the reaction conditions are extremely simple: to an equimolar mixture of arylidenalkylamine and ethylphenyl acetate, dissolved in undried benzene, was gradually added with stirring an equimolar amount of anhydrous aluminum chloride. The latter rapidly dissolved with the liberation of heat. Hydrochloric acid (1:1) was added to the cooled reaction mixture over a period of 15-20 minutes. The precipitated hydrochloride of the β -alkylamino ester was usually filtered on the following day. Only in the case of benzylidenethylamine was it necessary to heat the reaction mixture after the original exothermic heat of reaction faded in order to increase the yield of β -ethylamino ester. By this means, we prepared from the Schiff bases of benzaldehyde and β -naphthaldehyde with methylamine and ethylamine the hydrochlorides of the ethyl esters of α , β -diphenyl- β -methylamino-, α , β -diphenyl- β -ethylamino-, α -phenyl- β -(β -naphthyl)- β -methylamino-, and α -phenyl- β -(β -naphthyl)- β -ethylaminopropionic acids with yields of 18 to 41% of theory. These syntheses can be represented as follows:



In the reactions described, as in the case of the hydramides, it was necessary to use 1 mole of aluminum chloride per mole of starting materials. Probably, the use of equivalent quantities of reagents was dictated by the formation of more stable complexes between the anhydrous aluminum chloride and the products of the addition of ethyl acetate to such Schiff bases (A) or to the hydramide. These compounds are stronger bases than the products formed from Schiff bases of aniline. The formation of the intermediate product (A) is proposed also on the basis that anhydrous aluminum chloride dissolves in benzene solutions of free β -alkylamino esters (tested on a sample of ethyl α -phenyl- β -(β -naphthyl)- β -methylaminopropionate).

Preparation of the free β -alkylamino esters from their hydrochlorides by treatment of the latter with an

aqueous solution of sodium carbonate proceeded with quantitative yields.

Alkaline hydrolysis of the hydrochlorides of the ethyl esters of α , β -diphenyl- β -methylamino- and α , β -diphenyl- β -ethyl-aminopropionic acids gave the corresponding β -alkylamino acids (isolated as the hydrochlorides) with yields of 65 and 54% of theory.

With the aim of verifying the structures of the hydrochlorides of the ethyl esters of the β -alkylaminopropionic acids studied, the latter were converted, by boiling with a solution of potassium cyanate, into dihydrouracil derivatives, namely: 1-methyl-5,6-diphenyldihydrouracil, 1-ethyl-5,6-diphenyldihydrouracil, and 1-methyl-5-phenyl-6-(β -naphthyl)-dihydrouracil.

None of the compounds synthesized by us have been described in the literature.

It is our agreeable duty to express here our thanks to B.I. Kurtev for his interest and for his aid in the execution of this work.

EXPERIMENTAL

Ethyl α , β -diphenyl- β -methylaminopropionate hydrochloride. To a solution of 1.80 g (0.015 mole) of benzylidenemethylamine and 2.50 g (0.015 mole) of ethylphenyl acetate in 2 ml of undried benzene was added portion-wise and with stirring 2 g (0.015 mole) of powdered, anhydrous aluminum chloride. The latter quickly dissolved with the evolution of considerable heat. The cooled reaction mixture was stirred for 15-20 minutes with 20 ml of hydrochloric acid and allowed to stand overnight. The precipitated solid material was filtered and washed with ether. The yield was 1.20 g (28% of theory). M.p. 202-204°. The material was purified by dissolving in alcohol and precipitating with ether. The purified material melted at 205-206° (with decomposition).

Found %: N 4.28; 4.57

$C_{18}H_{22}O_2NCl$. Calculated %: N 4.38

The ethyl α , β -diphenyl- β -methylaminopropionate hydrochloride was colorless needles which were soluble in water and alcohol and insoluble in benzene and ether.

Ethyl α , β -diphenyl- β -methylaminopropionate. 20 ml of a 10% aqueous solution of sodium carbonate and 10 ml of ether were placed in a separatory funnel, 0.50 g of powdered ethyl α , β -diphenyl- β -methylaminopropionate hydrochloride was added, and the mixture was thoroughly shaken. The ether layer was separated, and the water layer was repeatedly extracted with ether. The combined ether extracts were dried with calcined sodium sulfate, and the ether was distilled off. An oily liquid remained which crystallized upon cooling with a mixture of ice and salt. The yield was 0.45 g (98% of theory). M.p. 32-35°. The material was purified by dissolving in a small quantity of alcohol and adding warm water until there appeared a turbidity which did not disappear on stirring. On cooling, an oil dropped out, and it completely solidified upon further cooling with an ice-salt mixture. M.p. of the purified preparation was 35-36°.

Found %: N 4.94

$C_{18}H_{21}O_2N$. Calculated %: N 5.18

The ethyl α , β -diphenyl- β -methylaminopropionate was a colorless, waxy substance, easily soluble in all the usual organic solvents and only slightly soluble in water.

α , β -Diphenyl- β -methylaminopropionic acid hydrochloride. A mixture of 0.50 g of the hydrochloride of the β -methylamino ester and a solution of 1 g of potassium hydroxide in 5 ml of alcohol and 3 ml of water was warmed on a water bath for 3 hours. The solution was then acidified with hydrochloric acid, evaporated to dryness, and the dry residue extracted several times with alcohol. 0.31 g (65% of theory) of a substance melting at 167-169° was precipitated with ether from the combined extracts. The material was purified by reprecipitating it several times from alcohol with ether. M.p. 190-191° (with decomposition).

Found %: N 4.73; 4.99

$C_{16}H_{15}O_2NCl$. Calculated %: N 4.80

The α , β -diphenyl- β -methylaminopropionic acid hydrochloride was in the form of colorless prisms which were insoluble in benzene and ether.

1-Methyl-5,6-diphenyldihydrouracil. A solution of 0.64 g (0.002 mole) of ethyl α , β -diphenyl- β -methylaminopropionate hydrochloride and 0.24 g (0.003 mole) of potassium cyanate in 3 ml of alcohol and 3 ml of water was warmed on a water bath for 2 hours; 2 ml of concentrated hydrochloric acid was then added, and the

solution was warmed for an additional half hour. After cooling the reaction mixture, the crystalline precipitate, which began to form while the solution was still warm, was filtered and washed with water and then with alcohol. M.p. 245-247°. After recrystallization from alcohol, the product melted at 247-248°.

Found%: N 9.99; 10.18

$C_{17}H_{16}C_2N_2$. Calculated %: N 10.00

The 1-methyl-5,6-diphenyldihydrouracil was in the form of colorless prisms which were soluble in hot alcohol and insoluble in benzene and ether.

Ethyl α , β -diphenyl- β -ethylaminopropionate hydrochloride. The preparation was carried out analogously to the preparation of the β -methylamino ester using equimolar quantities of benzylidenethylamine, ethylphenyl acetate, and anhydrous aluminum chloride in a medium of undried benzene. The total yield was 21% of theory. Following dissipation of the initial exothermic heat, the reaction mixture had to be heated for another 2 hours on a water bath at 50-55° in order to increase the yield of the β -ethylamino ester hydrochloride. After one recrystallization from alcohol, this hydrochloride was obtained in the form of needles with a m.p. of 205-206° (with decomposition).

Found %: N 4.44; 4.45

$C_{19}H_{24}O_2NCl$. Calculated %: N 4.20

Ethyl α , β -diphenyl- β -ethylaminopropionate. This compound was obtained with a yield of 93% of theory by treating its hydrochloride with a solution of sodium carbonate according to the above-described method. After one recrystallization from benzene, the material was obtained in the form of colorless prisms having a m.p. of 55-56°.

Found%: N 4.99

$C_{19}H_{22}O_2N$. Calculated%: N 4.71

α , β -Diphenyl- β -ethylaminopropionic acid hydrochloride. A mixture of 0.50 g of the β -ethylamino ester hydrochloride with 4 ml of a 30% solution of sodium hydroxide and 5 ml of alcohol was warmed for 2 hours on a boiling water bath. The reaction mixture was treated in the manner described for the preparation of α , β -diphenyl- β -methylaminopropionic acid hydrochloride. The yield of raw product was 0.25 g (54% of theory). M.p. 182-183°. The α , β -diphenyl- β -ethylaminopropionic acid hydrochloride, purified by reprecipitation from alcohol with ether, was in the form of colorless prisms with a m.p. of 183-184° (with decomposition).

Found %: N 4.45; 4.67

$C_{17}H_{16}O_2NCl$. Calculated %: N 4.58

1-Ethyl-5,6-diphenyldihydrouracil. From 0.33 g (0.001 mole) of ethyl α , β -diphenyl- β -ethylaminopropionate hydrochloride and 0.12 g (0.0015 mole) of potassium cyanate there was obtained, by the above-described method (warming time 4 hours), 0.10 g (34% of theory) of raw 1-ethyl-5,6-diphenyldihydrouracil with a m.p. of 228-230°. A single recrystallization from alcohol gave a product melting at 231-232°.

Found %: N 9.25; 9.47

$C_{18}H_{18}O_2N_2$. Calculated %: N 9.52

Ethyl α -phenyl- β -(β -naphthyl)- β -methylaminopropionate hydrochloride. The method of preparation of this material was analogous to the synthesis of α , β -diphenyl- β -methylaminopropionic acid hydrochloride (the ethyl ester was probably meant). Treatment of the reaction mixture was carried out with warming to accelerate the hydrolysis of the unreacted Schiff base. From 0.85 g (0.005 mole) of β -naphthylidenmethylamine [3], 0.81 g (0.005 mole) of ethylphenyl acetate, and 0.70 g (0.005 mole) of anhydrous aluminum chloride there was obtained 0.67 g (41% of theory) of raw ethyl α -phenyl- β -(β -naphthyl)- β -methylaminopropionate with a m.p. of 197.5-199°. The product, after purification by a single reprecipitation from alcohol with ether, had a m.p. of 198-199° (with decomposition).

Found %: N 3.97; 4.11

$C_{22}H_{24}O_2NCl$. Calculated %: N 3.79

Ethyl α -phenyl- β -(β -naphthyl)- β -methylaminopropionate. The raw product, obtained by the above-described method with a yield of 96% of theory, had a m.p. of 82-84°. After one recrystallization from benzene, the colorless needles melted at 87.5-88.5°.

Found %: N 4.49
 $C_{21}H_{23}O_2N$. Calculated %: N 4.20

1-Methyl-5-phenyl-6-(β -naphthyl) dihydrouracil. This compound was obtained analogously to the above-described dihydrouracil derivative (warming time 1 hour). The yield was 44% of theory. M.p. of the raw product was 246-248°. The preparation was recrystallized from alcohol, and the colorless prisms melted at 252-253°.

Found %: N 8.65; 8.68
 $C_{21}H_{19}O_2N_2$. Calculated %: N 8.48

β -Naphthylidenethylamine. This compound was prepared from equimolar quantities of β -naphthaldehyde [3], ethylamine hydrochloride, and potassium hydroxide by a method analogous to the preparation of β -naphthylidenemethylamine [3]. The β -naphthylidenethylamine was recrystallized several times from benzene, and the colorless plates melted at 62.5-63°.

Found %: N 8.04; 7.87
 $C_{13}H_{13}N$. Calculated %: N 7.65

Ethyl α -phenyl- β -(β -naphthyl)- β -ethylaminopropionate hydrochloride. This material was obtained analogously to the synthesis of the β -methylamino ester hydrochloride. The yield was 18% of theory. The preparation, purified by recrystallization from alcohol with ether, was in the form of colorless prisms with a m.p. of 177-178° (with decomposition).

Found %: N 3.78; 3.93
 $C_{23}H_{25}O_2NCl$. Calculated %: N 3.65

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ISOTHIOCYANONITRO- AND ISOTHIOCYANOHALO-BIS-DIMETHYLGLY- OXIMCOBALTIC ACIDS

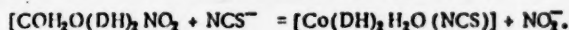
A.V. Ablov, N.M. Samuc and M.S. Popov

(Presented by Academician I.N. Nazarov, July 2, 1955)

In an article by one of us [1], it was shown that the action of hydrochloric or hydrobromic acid on nitro-bis-dimethylglyoximaquocobalt forms, respectively, chloronitro- or bromonitro-bis-dimethylglyoximcobaltic acid.

Upon warming nitro-bis-dimethylglyoximaquocobalt with a solution of 1 equivalent of potassium isocyanate, the difficultly soluble nitroquo compound goes into solution. If several drops of ammonia are added to the dark brown solution to make it weakly alkaline, yellowish brown crystals of the composition $[\text{Co}(\text{DH})_2(\text{NCS})] \cdot \text{H}_2\text{O}$ precipitate in almost quantitative yield. The latter compound has already been described [2] and the assumption was made that an isothiocyano group was connected to the cobalt through the nitrogen atom.

The formation of the isothiocyanoquo compound from the nitro-bis-dimethylglyoximaquocobalt proceeds according to the equation:

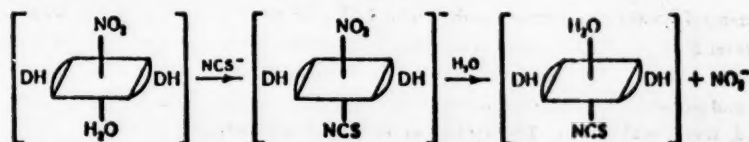


However, it is impossible to reconcile the assumption that the mechanism of the reaction leads to substitution of the nitro group by the isothiocyano group with the facts known from the chemistry of complex cobalt compounds. More probable is the assumption that, by analogy with the reaction of the nitroquo compound with hydrogen halide acids, the molecule of water is substituted by the isothiocyano group with the formation of the intermediate anion $[\text{Co}(\text{DH})_2(\text{NO}_2)\text{NCS}]^-$, which then rearranges into isothiocyano-bis-dimethylglyoximaquocobalt.

In previous work [3-5], it was shown that the anion $[\text{Co}(\text{DH})_2\text{X}_2]^-$ (where $\text{X} = \text{NO}_2, \text{Br}, \text{Cl}$) gives with cations having the composition $[\text{Co}(\text{Amin})_2(\text{DH})_2]^+$ difficultly soluble crystalline precipitates. Upon the addition of $[\text{Co}(\text{Amin})_2(\text{DH})_2]\text{X}_2$ (where Amin = pyridine or o-toluidine) to the dark brown solution obtained by warming nitro-bis-dimethylglyoximaquocobalt with potassium isothiocyanate, a precipitate which includes the isothiocyanonitrate anion is obtained.

Upon acidification to a strongly acid reaction (pH 2 - 3) of the solution obtained by warming the nitroquo compound with potassium isothiocyanate, crystals of isothiocyanonitro-bis-dimethylglyoximcobaltic acid separate. In water solution, with the addition of ammonia it is converted at ordinary temperatures into the isothiocyanoquo compound.

If the trans configuration of cobalt dioximes is taken as the more probable [1], the formation of isothiocyano-bis-dimethylglyoximaquocobalt from the nitroquo compound proceeds in the following manner.



This course of the reaction is fully explained by the rule of trans effect of I.I. Chernyaev, if it is assumed that the isothiocyano group in cobalt dioximes has a strong trans effect.

In isothiocyano-bis-dimethylglyoximaquocobalt, just as in the nitroquo compound, the water molecule must be labilized in conformity with the rule of trans effect: [6], and must be capable of substitution by other groups. Actually, in the action of concentrated hydrochloric and hydrobromic acids on isothiocyanoquo compounds, with warming, the water molecule is substituted by HCl or HBr, respectively.

The materials obtained, $\text{H}[\text{Co}(\text{DH})_2(\text{NCS})\text{Cl}] \cdot \text{H}_2\text{O}$ and $\text{H}[\text{Co}(\text{DH})_2\text{NCSBr}] \cdot \text{H}_2\text{O}$, are crystalline products, very unstable toward water in which they dissolve completely with the formation of isothiocyanoquo compounds.

Upon comparing the ease of hydration of nitrohalo- and isothiocyanohalocobaltic acids, it becomes apparent why, in the second case, washing out of the halogens proceeds considerably more easily. This gives reason to assume that, in cobalt dioximes, the isothiocyano group precedes the nitro group in trans activity.

EXPERIMENTAL

Isothiocyano-bis-dimethylglyoximaquocobalt $[\text{CoH}_2\text{Q}(\text{DH})_2\text{NCS}] \cdot \text{H}_2\text{O}$.

3.5 g (0.01 mole) of nitro-bis-dimethylglyoximaquocobalt and 0.97 g of potassium thiocyanate in 100 ml of water were warmed on a water bath. The nitroquo compound gradually went into solution giving a dark brown color. The reaction was concluded in 45-60 minutes.

To the still warm, filtered solution was added several drops of concentrated ammonia (to a weakly alkaline reaction). After several minutes, a copious precipitate separated, which was filtered and washed with cold water and alcohol. The yield was 80-90% of theoretical.

The yellowish brown crystalline powder, when examined under the microscope, had the form of tetragonal prisms with beveled faces. The material was almost insoluble, in water and organic solvents.

Found %: Co 15.33; 15.38; N 18.48; S 7.87; H_2O 5.32; 4.88
 $[\text{CoH}_2\text{Q}(\text{DH})_2(\text{NCS})] \cdot \text{H}_2\text{O}$. Calculated %: Co 15.38; N 18.27; S 8.34; H_2O 4.70

Isothiocyanonitro-bis-dimethylglyoximcobaltate bis-dimethyl-glyoximdipyridin-cobalt $[\text{CoPy}_2(\text{DH})_2][\text{Co}(\text{DH})_2(\text{NCS})\text{NO}_2]$.

1.75 g of nitroquo compound was warmed on a water bath with a solution of 0.48 g of potassium thiocyanate in 100 ml of water. To the warm, filtered solution was added 2.5 g of dipyrind-bis-dimethylglyoximcobaltichloride in 75 ml of 50% alcohol. Upon cooling, a yellow, finely crystalline precipitate separated, which was filtered and washed with cold water and alcohol. The yield was 70-80% of theoretical.

Under the microscope, the crystals had the form of irregular, short hexagonal prisms. The material was difficultly soluble in water and alcohol.

Found %: Co 13.96; 13.90; 13.78; N 19.90; NCS 7.10; 7.18
 $[\text{Co}(\text{C}_5\text{H}_5\text{N})_2(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2][\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{NCS})\text{NO}_2]$.
 Calculated %: Co 14.02; N 19.98; NCS 6.91

Isothiocyanonitro-bis-dimethylglyoximcobaltate bis-dimethylglyoximdio-toluidin-cobalt $[\text{Co}(\text{O}-\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_3)_2][\text{Co}(\text{DH})_2(\text{NCS})\text{NO}_2]$.

The method of preparation was analogous to the preceding.

Under the microscope, the fine, light brown crystals had the form of tetragonal plates.

Found %: Co 12.97; 13.00; 13.08; NCS 6.39; 6.65
 $[\text{Co}(\text{C}_7\text{H}_7\text{N}_2)(\text{C}_6\text{H}_4\text{N}_2\text{O}_2)_2][\text{Co}(\text{C}_6\text{H}_4\text{N}_2\text{O}_2)_2(\text{NCS})\text{NO}_2]$. Calculated %: Co 13.14; NCS 6.48

Isothiocyanonitro-bis-dimethylglyoximcobaltic acid $\text{H}[\text{Co}(\text{DH})_2(\text{NCS})\text{NO}_2] \cdot \text{H}_2\text{O}$.

3.5 g of nitro-bis-dimethylglyoximaquocobalt and 0.97 g of potassium thiocyanate were warmed with 100 ml of water on a water bath until the nitroquo compound dissolved. Upon acidification of the cooled solution with 50% sulfuric acid to a pH of 2-3, a cherry brown, finely crystalline precipitate separated, which was slowly filtered by suction and pressed several times between sheets of filter paper. Under the microscope, the material took the form of red, tetragonal prisms. The yield was 40-50% of theoretical.

Found %: Co 14.19; NCS 14.24; N 19.97; H₂O 4.23
H[Co(C₄H₇N₂O₂)₂(NCS)NO₂]·H₂O. Calculated %: Co 14.29; NCS 14.09; N 20.39; H₂O 4.37

The isothiocyanonitro compound was easily soluble in alcohol. When water was poured over it, the color changed to yellow. If the isothiocyanonitro compound was drenched with a dilute solution of ammonia at room temperature, it was quantitatively converted into a yellowish brown crystalline material, the color, crystalline form, and composition of which completely corresponded with those of an isothiocyanoaquo compound.

1.0022 g of isothiocyanonitrocobaltic acid, H[Co(DH)₂(NCS)NO₂]·H₂O, gave 0.9042 g of air-dried isothiocyanoaquo compound, [Co(H₂O(DH)₂·(NCS))]·H₂O, (theoretical, 0.9315 g).

Found %: N 18.63
[CoH₂O(C₄H₇N₂O₂)₂(NCS)]·H₂O. Calculated %: N 18.27

Chloroisothiocyano-bis-dimethylglyoximcobaltic acid H[Co(DH)₂(NCS)Cl]·H₂O.

3 g of powdered isothiocyanoaquo compound was drenched in a beaker with concentrated hydrochloric acid. The contents of the beaker were warmed on a water bath until the yellowish brown precipitate had not quite changed to a brownish red. After cooling, the material was suction filtered on a glass filter and washed with concentrated hydrochloric acid. The material was dried in an atmosphere of hydrogen chloride in a desiccator over concentrated sulfuric acid. Under the microscope, the yellowish red, finely crystalline powder had the form of octahedrons. The yield was 60% of theoretical. If the material was drenched with water or alcohol, the color immediately changed to yellow owing to the formation of the isothiocyanoaquo compound.

Found %: Co 14.46; 14.41; NCS + Cl 23.76; 23.72; H₂O 5.04
H[Co(C₄H₇N₂O₂)₂(NCS)Cl]. Calculated %: Co 14.67; NCS + Cl 23.28; H₂O 4.48

Bromoisothiocyano-bis-dimethylglyoximcobaltic acid H[Co(DH)₂(NCS)Br]·H₂O.

The material was prepared analogously to the chloro derivative with a yield of 60%. It was dried in an atmosphere of hydrogen bromide in a desiccator over concentrated sulfuric acid. Under the microscope, the dark red crystals had the form of octahedrons.

Found %: Co 13.19; 13.14; NCS + Br 30.70; 30.74; H₂O 4.88; 4.26
H[Co(C₄H₇N₂O₂)₂(NCS)Br]·H₂O. Calculated %: Co 13.21; NCS + Br 30.93; H₂O 4.03

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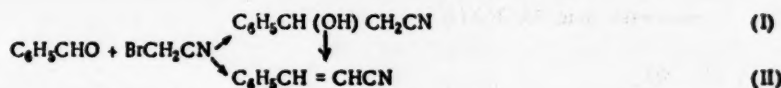
CONDENSATION OF BENZALDEHYDE WITH BROMOACETONITRILE

N.S. Vulfson and L.Kh. Vinograd

(Presented by Academician I.N. Nazarov, May 20, 1955)

The Reformatsky reaction, a reaction of β -haloesters of carboxylic acids with aldehydes, ketones, or esters in the presence of zinc, is widely used in preparative organic chemistry [1,2]. In recent years, work has appeared on modifications of this reaction and on its extension to other classes of compounds. Thus, acyl chlorides have been used as the component containing the carbonyl group [3]. The effect of different catalysts and solvents has also been studied [4]. Up to the present time, only β -haloesters and their vinylogs have been used as the second component of the reaction.

Since the possibility of substituting β -halonitriles for the β -haloesters appeared to be of interest, we decided to carry out the condensation of benzaldehyde with bromoacetonitrile under the usual Reformatsky reaction conditions. Literature data on this question, which was interesting to us, were non-existent; however, it could be assumed that the result of the reaction would be the formation of either β -hydroxy- β -phenylpropionitrile or cinnamonitrile:



The reaction product was a colorless, viscous, odorless liquid. B.p. 147-151° at 4-5 mm; n_D^{20} 1.5388, d_4^{20} 1.1179. Since the properties of cinnamonitrile (II) (b.p. 134-136° at 12-13 mm, d_4^{20} 1.037 [5]) differ considerably from those found, we assigned to the reaction product the structure β -hydroxy- β -phenylpropionitrile (I). This structure is confirmed by data from elemental analysis, by the agreement of the observed molecular refraction (40.208) with the calculated value (40.504), by the absence of a double bond [6] (does not add halogen), by a determination of the hydroxyl number [7] (acetylation with acetic anhydride in pyridine solution), by saponification to the previously described amide [8], and also by conversion to cinnamic acid by boiling with sodium hydroxide. This compound was previously prepared [8] by the reduction of ω -cyanoacetophenone with sodium amalgam, but, except for conversion to the amide, it was not identified.

EXPERIMENTAL

To a boiling mixture of 21.3 g of carefully dried benzaldehyde, 32 ml of benzene, 8 ml of ether, and 18 g of activated zinc dust [2] was added, over a 30-minute period, 24 g of bromoacetonitrile [9] (d_4^{20} 1.810). The mixture was boiled for 2 hours, cooled to room temperature, and stirred for 1 hour with 120 ml of 10% sulfuric acid (the temperature was about 35°). An insignificant amount of solid residue was filtered off, and the benzene layer was separated and washed with 10% sulfuric acid and water. The water layer and the acid wash water were extracted with benzene which, after washing, was added to the main body of benzene. The benzene and ether were distilled off, and the residue was distilled under a vacuum of 4-5 mm. The first fraction (0.9 g), b.p. 50-135°, had the odor of benzaldehyde, and was a mixture of the latter with β -hydroxy- β -phenylpropionitrile; the second fraction was pure β -hydroxy- β -phenylpropionitrile, b.p. 147-151° at 4-5 mm, 14.2 g.

Found %: C 73.21; 72.92; H 6.22; 6.29; N 9.40; 9.37
C₉H₉ON. Calculated %: C 73.41; H 6.16; N 9.57

The hydroxyl number (two determinations) was 379.6 and 386.07 (calculated 381.3).

Preparation of the amide [10]. 0.08 g of β -hydroxy- β -phenylpropionitrile was vigorously agitated for 30 minutes at 40-50° with 1.5 ml of 12% hydrogen peroxide in the presence of one drop of 1 N potassium hydroxide and 0.5 ml of alcohol, and allowed to stand overnight. The precipitated crystals were filtered, washed with ether, and recrystallized from alcohol. M.p. 120°.

Saponification with alkali. 0.3154 g of β -hydroxy- β -phenylpropionitrile was boiled for 4 hours with 20 ml of 4 N sodium hydroxide. The liberated ammonia was absorbed in 0.1 N hydrochloric acid, and the excess acid was back-titrated with 0.1 N sodium hydroxide. 0.0353 g of ammonia was liberated - 96.98% of theory. The residue in the flask was acidified with concentrated hydrochloric acid and left overnight. The resulting cinnamic acid was filtered and washed with water. 0.2025 g of the acid was obtained - 63.65% of theory, m.p. 133-133.5°.

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AROMATIC HYDROCARBONS IN BAVLINSK KEROSENE

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The subject of the investigation which has been carried out is the aromatic hydrocarbons of the kerosene fractions of the most promising petroleum of the Tartar ASSR — petroleum of the Bavlinsk formation. The full-range Bavlinsk kerosene, boiling at 180-300°, had the following properties: d_4^{20} 0.8269, n_D^{20} 1.4610, freezing point -26°, and sulfur content 0.69%.

The kerosene was distilled in a fractionating column into 5 fractions which are characterized in Table 1.

In order to separate the aromatic hydrocarbons from the kerosene fractions, each of them, except the first, was subjected to adsorption on silica gel (50-80 mesh). As a result of adsorption of the aromatic hydrocarbons on silica gel (135-200 mesh), fractions were removed from the column in the order of increasing adsorbability (A_I , A_{II} , A_{III}). Fused-ring hydrocarbons of the naphthalene series were investigated. Simultaneously, the main body of aromatic hydrocarbons, represented by various types, were also characterized.

In the study of aromatic hydrocarbons of the naphthalene series of Bavlinsk kerosene, we used the picrate method developed by Cosciug [1] in the significantly supplemented and improved form developed by S. S. Nametkin, E. S. Pokrovskaya and T. G. Stepantseva [2].

During the investigation of the naphthalenic hydrocarbons by treatment with picric acid, not the kerosene fraction but only the aromatic fractions, represented chiefly by a single type of hydrocarbon, were subjected to the treatment. The naphthalene homologs, which were isolated through the picrates from the aromatic fractions, were separated into solid and liquid portions by fractional freezing.

Comparing the constants of the isolated hydrocarbons with those of individual hydrocarbons leads to the following conclusions:

1. A substance melting at 80-81° was isolated from the 176-207° fraction; its picrate melted at 148-149°. These data correspond to naphthalene (b.p. 218°, m.p. 80.3°, m.p. of the picrate 149.5° [8]).

2. A solid and a liquid were obtained from the 207-232° fraction. The m.p. of the solid was +34°, and the m.p. of its picrate was 114.5°. Its composition was $C_{11}H_{10}$.

Found %: C 92.83; 92.74; H 7.3; 7.27
 $C_{11}H_{10}$. Calculated %: C 92.91; H 7.09

This crystalline substance was β -methylnaphthalene (b.p. 241°, m.p. +34.5° m.p. of the picrate 116-117° and 115.8° [3,4]).

The liquid material, after repeated freezing, had a freezing point -33°, d_4^{20} 1.0146, n_D^{20} 1.6014, m.p. of the picrate 119.5-120.5°.

The freezing point of this hydrocarbon agrees well with that of α -methylnaphthalene, but the lower melting point of its picrate (119.5-120.5°), on comparison with that for pure α -methylnaphthalene (141.5° [5]), corresponds to a mixture of the picrates of α - and β -methylnaphthalene. By spectral analysis, the liquid material was determined to be a mixture of isomers with a clear preponderance of β -methylnaphthalene.

3. From the 233-249° fraction was obtained a crystalline material with the odor of anise, m.p. 108-109°, m.p. of the picrate 139.5-140.5°. Its composition was $C_{12}H_{12}$.

Found %: C 92.37; H 7.68
 $C_{12}H_{12}$. Calculated %: C 92.26; H 7.74

Literature data for 2,6-dimethylnaphthalene are: b.p. 261°, m.p. 110-111°, and m.p. of the picrate 141-142° [5]. Therefore, the crystalline hydrocarbon was 2,6-dimethylnaphthalene.

Properties of the liquid material were: b.p. 262-264°, d_4^{20} 1.0144, n_D^{20} 1.6000, f.p. -50°, and m.p. of its picrate 112-114°. Its properties approach those of 1,6- and 1,7-dimethylnaphthalene. (For 1,7-dimethylnaphthalene: b.p. 263°, f.p. -14 and -28°, d_4^{20} 1.0115, n_D^{20} 1.6083, m.p. of the picrate 118.5°, 123-124° [4]. For 1,6-dimethylnaphthalene: b.p. 262-263°, f.p. -17 and -15°, d_4^{20} 1.0017, n_D^{20} 1.6072, m.p. of the picrate 110-111°, 112°, 113°, 114° [5].) The low melting point of the material is explained, apparently, by the presence of two isomers, 1,6- and 1,7-dimethylnaphthalene.

TABLE 1

Properties of Aromatic Hydrocarbons from Bavlinsk Kerosene (after removal of the naphthalene)

Properties of the kerosene fractions	Fraction	B.p. in °C and pressure in mm Hg	d_4^{20}	n_D^{20}	Specific depression $\frac{n_F - n_C}{d}$	Refractivity intercept $n - \frac{d}{2}$
B.p. 207-232° d_4^{20} 0.8110, n_D^{20} 1.4535 F.p. -39°	A _I	107-128.5 (20 mm)	0.8859	1.5007	152.6	1.0578
	A _{II}	102-118 (17 mm)	0.9066	1.5143	165.7	1.0610
	A _{III}	107-130 (21 mm)	0.9202	1.5255	176.6	1.0654
B.p. 233-249° d_4^{20} 0.8280, n_D^{20} 1.4623 F.p. -25°	A _I	126-135 (18 mm)	0.8896	1.5043	—	1.0595
	A _{II}	132-133 (22-19 mm)	0.9119	1.5165	161.0	1.0606
	A _{III}	124-126 (16-15 mm)	0.9184	1.5183	162.2	1.0641
	A _{IV}	135-138 (17 mm)	0.9391	1.5305	171.7	1.0710
B.p. 249-270° d_4^{20} 0.8347, n_D^{20} 1.4663 F.p. -20°	A _I	131-137 (14 mm)	0.8934	1.5050	155.5	1.0583
	A _{II}	127-141 (11 mm)	0.9117	1.5163	167.1	1.0605
	A _{III}	136-137 (14-13.5)	0.9470	1.5370	181.6	1.0635
		142-143 (14.5 mm)	0.9498	1.5410	186.0	1.0661
B.p. 270-300° d_4^{20} 0.8395, n_D^{20} 1.4680 F.p. -11°	A _I	123-121.5 (3-1.5 mm)	0.8954	1.5036	148.1	1.0559
	A _{II}	118-126 (2.5 mm)	0.9143	1.5168	162.0	1.0597
	A _{III}	101-110 (2 mm)	0.9186	1.5200	162.3	1.0607
		96-98 (1 mm)	0.9543	1.5432	176.4	1.0661
		114-118.5 (1.5 mm)	0.9563	1.5430	188.6	1.0649

The study of the naphthalenic hydrocarbons in the 249-270° and 270-300° fractions was carried out after fractional distillation into a series of narrow and compositionally similar fractions.

A solid and a liquid material were isolated from the 116-126° (13 mm) fraction. The solid substance melted at 70-71°, and its picrate, in the form of long, golden needles, melted at 102-103°. Elemental analysis showed that its composition corresponded to a dimethylnaphthalene:

Found %: C 92.22; 92.34; H 7.7; 7.68
 $C_{12}H_{12}$ Calculated %: C 92.25; H 7.79

However, its properties did not approach those given in the literature for any dimethylnaphthalene isomer. The structure of this material was definitely established by spectral analysis, which confirmed that it was an eutectic mixture of the two solid 2,6- and 2,3-isomers.

The liquid product remaining after the removal of the crystals had the properties: d_4^{20} 1.0110, n_D^{20} 1.6082, f.p. -55°, m.p. of the picrate 115-116°. The low freezing point, not characteristic of naphthalene homologs, was apparently attributable to the presence of a mixture of hydrocarbons of various structures. As shown by

spectral analysis, this material was mainly 1,7- and 1,3-dimethylnaphthalenes with some admixture of 1,2-dimethylnaphthalene.

An oil, b.p. 143-144° (13 mm), was obtained from the 133-142° (13 mm) fraction, and was separated into a solid and a liquid material. The crystals had the form of lustrous plates with a weakly aromatic odor, m.p. 100.5-101.5°, m.p. sec. picrates 130°.

Found %: C 91.47; H 8.54
 $C_{13}H_{14}$. Calculated %: C 91.71; H 8.29

This material was 2,3,6-trimethylnaphthalene (b.p. 146-148°, (14 mm), m.p. 102°, m.p. [picrate] 130° [6]).

Properties of the liquid were: d_4^{20} 1.0076, n_D^{20} 1.6050, m.p. of the picrate 114-116°; thus, it closely approached 1,3,6-trimethylnaphthalene (b.p. 140-144° (10 mm), m.p. [picrate] 114-115° [7]).

The presence of solid and liquid homologs of naphthalene in the 270-300° fraction was established. In one and the same fraction, 133-138° (12 mm), were present:

1) Crystalline 2,3,6-trimethylnaphthalene, the properties of which compared accurately with those of the hydrocarbon isolated from a previous fraction.

2) A liquid product, the picrate of which melted at 115-117° and the elemental composition of which corresponded to a mixture of tri- and tetramethylnaphthalene:

Found %: C 91.39; 91.42; H 8.64; 8.62
 $C_{13}H_{14}$. Calculated %: C 91.71; H 8.29
 $C_{14}H_{16}$. Calculated %: C 91.24; H 8.76

In addition, from the 138-143° and 143-148° (12 mm) fractions tetramethylnaphthalene was isolated as solid and liquid.

When melted in a capillary, the solid melted stepwise, the first part at 106-107° and the second, finally, at 144°. Apparently, it comprised a mixture of solid tetramethylnaphthalenes; this appeared more probable when elemental analysis of the liquid, after removal of crystalline material, corresponded to tetramethylnaphthalene.

Properties of the liquid were: d_4^{20} 1.0147, n_D^{20} 1.6010, m.p. of the picrate 125-127°.

Found %: C 91.23; 91.39; H 8.8; 8.73
 $C_{14}H_{16}$. Calculated %: C 91.24; H 8.76

The lowered melting points for the tetramethylnaphthalene picrates [3,8] can be explained on the basis that the hydrocarbons isolated from a given fraction were a mixture of structural isomers.

Thus, it was established that Bavlinsk kerosene boiling at 176-300° contains the following: naphthalene, α - and β -methylnaphthalene, 2,6- and 2,3-, 1,6- and 1,7-, and 1,3-dimethylnaphthalenes, 2,3,6- and 1,3,6-trimethylnaphthalenes, and tetramethylnaphthalenes of unknown structure. The naphthalene homologs comprise, on the average, 11 to 20% of the aromatic hydrocarbons. The physicochemical properties of the aromatic fractions, after they have been freed from naphthalenic hydrocarbons, are given in Table 1.

From the table it follows that A_I in all four kerosene fractions comprised mainly benzene homologs; A_{II} and A_{III} in the same fractions comprised mainly mixtures of alkylbenzenes and hydrocarbons of the naphthene-aromatic series with a predominance of the latter.

Common to all of the isolated aromatic fractions was the presence of naphthenic rings, which was established by the method of Martin and Sankin. The average number of naphthenic rings per molecule in fraction A_I was 0.35-0.5, A_{III} 0.48-0.78, while the number of aromatic rings was A_I 0.9-1.04, and A_{III} 1.12-1.23.

It was established that the distribution of naphthalenic hydrocarbons in A_I , A_{II} , and A_{III} in all kerosene fractions was: A_I , completely absent; A_{II} , small amount (not more than 2%); A_{III} , characterized by a concentration of all homologs of naphthalene.

This investigation has shown that it is possible to isolate from sulfur-containing Tartar petroleum individual hydrocarbons of the naphthalene series, free from sulfur, and to identify them.

The investigation of Bavlinsk kerosene showed the complexity of the aromatic portions of the fractions, both with regard to diversity of hydrocarbon types and with regard to the structures of the naphthalenic hydro-

carbons*.

In conclusion, we express our appreciation to Academician B.A. Arbuzov for valuable advice.

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*Spectral analysis of three hydrocarbons and elemental analysis of isolated hydrocarbons were carried out in the Petroleum Institute of the Academy of Science USSR.

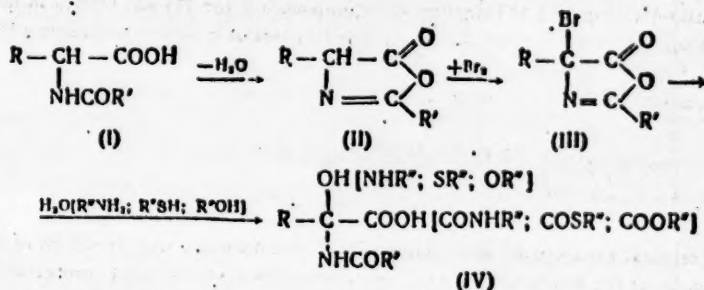
SYNTHESIS OF α -SUBSTITUTED α -AMINO ACIDS AND THEIR DERIVATIVES

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Recently, we described [1,2] a route for the synthesis of α -hydroxy- α -acylamino acids (IV) which permits the preparation of these compounds starting with the N-acylated α -amino acid (I) and proceeding through the corresponding oxazolinone (II) and bromoxazolinone (III). Now we have established that this route has a far broader significance inasmuch as it has been shown that it is possible to think of it as a basic, general method for the synthesis of the most varied α -substituted α -acylamino acids and their derivatives. Owing to the possibility of reacting the intermediate bromoxazolinone (III) both with water and with amines, mercaptans, or alcohols, it is easily possible to introduce at the α -carbon atom of the α -acylamino acids not only HO- but also RNH-, RS- or RO-groups. By the action of an excess of the reagent, in the three latter cases, the α -substituted α -acylamino acids are usually obtained in the form of the corresponding derivatives at the carboxyl group.

Scheme 1



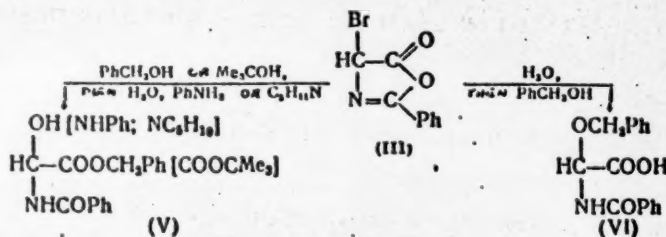
R = H, CH₃; R' = C₆H₅; R'' = CH₃, C₄H₉, (CH₃)₂CH, (CH₃)₃CH, CH(CH₃)₂, C(CH₃)₃, C₆H₁₁, CH₂C₆H₅, C₆H₅.

Thus, 4-bromo-2-phenyloxazolinone reacting with aniline gives α -phenylamino- α -benzoylamino-acetanilide (Compound 18; see Table 1), reacting with benzylmercaptan gives the benzyl ester of α -benzylmercapto- α -benzoylaminothiolacetic acid (Compound 19), and reacting with alcohols (alcoholates are not as good [1]) gives esters of α -alkoxy- α -benzoylaminoacetic acids (Compounds 1-8). The latter reaction was studied by us in the greatest detail. The reaction is easily carried out by mixing for 1 hour a dichloroethane solution of the bromoxazolinone with an excess of absolute alcohol. This reaction proceeds under almost identical conditions for primary and secondary aliphatic, alkyl-aromatic, and alicyclic alcohols (methyl, ethyl, propyl, isopropyl, lauryl, benzyl, and cyclohexyl alcohol), and the yields of the product esters (Compounds 1-5, 7, and 8) usually reach 40-60%, and only for Compound 10 was the yield less than 30%. In the case of tertiary butyl alcohol, along with the corresponding ester of the α -alkoxy- α -benzoylaminoacetic acid, (Compound 6), Compounds 11 and 14 were also obtained; in the case of phenol, the phenyl ester of N-benzoylhydroxyglycine (Compound 9) was also isolated.

During the study of reactions of the bromoxazolinones with alcohols, we observed that breaking of the oxazolinone ring proceeded more quickly than substitution of the bromine atom by the alkoxy group; an analogous phenomenon was recently noted in other instances by I.L. Knunyants and co-workers [3]. We used this

difference in the reactivity of the oxazolinone ring and the bromine atom for the synthesis of α -substituted α -acylamino acids and their derivatives (for example, of the type of V and VI) which could not be prepared by Scheme 1. In a series of instances, the reaction could be carried out in two stages – first, opening of the oxazolinone ring under mild conditions; second, exchange of the required substituent for the bromine atom by reaction with another reagent (see Scheme 2).

Scheme 2



Thus, by the action of 1 mole of benzyl alcohol on bromoxazolinone (III) at 0° and then treating with an excess of water, the benzyl ester of N-benzoylhydroxyglycine (Compound 13) was obtained, and by the substitution of aniline or piperidine for water, the benzyl ester of α -phenylamino- (or α -piperidyl-) α -benzoylaminoacetic acid (Compounds 15 and 16) was obtained. When the order of addition of reagents was reversed (first, 1 mole of water at 0°; then benzyl alcohol), O-benzyl-N-benzoylhydroxyglycine (Compound 12) was formed. Analogous results were obtained by the action of absolute trimethylcarbinol on bromoxazolinone (III) followed by water or aniline; Compound 14 (together with Compounds 6 and 11) was formed in the first case and Compound 17 in the second. On the other hand, Compound 11 was obtained in particularly high yield (reaching 50%) when the bromoxazolinone (III) reacted with trimethylcarbinol containing 3.5% water, which was able to split the oxazolinone ring much more vigorously than the tertiary alcohol.

EXPERIMENTAL

1. Preparation of Compounds 1-8. To a solution of 5 g of 2-phenyloxazolinone-5 in 33 ml of dry dichloroethane was added dropwise 2.5 g of bromine in 7 ml of dichloroethane at 5°. The precipitated crystals of hydrobromide of the original oxazolinone were quickly filtered and washed with 15-20 ml of dichloroethane [1]. The dichloroethane solution of the 4-bromo-2-phenyloxazolinone-5 was stirred, while protected from atmospheric moisture, for 1 hour at 25-28° with the corresponding absolute alcohol, using 1.5 moles for Compounds 4, 7, and 8 and 5-8 moles for Compounds 1, 2, 3, 5, and 6, these quantities being per mole of initial 2-phenyloxazolinone-5. The resulting solution was washed twice with water, dried over Na_2SO_4 , evaporated under vacuum (ending at 40-50°), mixed with 10 ml of ether, and the residue was filtered and recrystallized as stated in the table.

2. Preparation of Compound 10. The initial 4-methyl-2-phenyloxazolinone-5 was brominated under previously described conditions [1], and the reaction with CH_3OH was carried out as in Experiment 1 but at 18-20° for 5 hours.

3. Preparation of Compounds 6, 11, and 14 was carried out under the conditions of Experiment 1 using 6 g of absolute trimethylcarbinol. After the addition of 10 ml of ether, 1.1 g (23%) of Compound 6 was filtered off, and the ethereal filtrate was extracted with an 8% solution of NaHCO_3 . The water solution was acidified, and 0.35 g (9%) of Compound 11 was filtered off; after evaporation of the ethereal solution, 1.55 g (39%) of Compound 14 was isolated.

If the reaction was carried out with 6 g of trimethylcarbinol containing 3.5% water, then, when the reaction mixture was washed with water, Compound 11 was liberated, and was filtered off and washed with water. The amount was 2 g (48%). The material was crystallized from 70% $\text{C}_2\text{H}_5\text{OH}$ as the monohydrate which melted at 103-104°, resolidified at about 140°, and melted a second time, with decomposition, at 201°.

TABLE 1

 α -Substituted α -Amino Acids and Their Derivatives

Preparation No.	Compound	M.p. °C and solvent for the crystallization	Yield %*	Calculated %			Found %		
				C	H	N	C	H	N
1	OCH_3 BzNHCHCOOCH_3	86—87 Et_2O	56	59.19	5.87		59.00	5.72	
2	OC_2H_5 $\text{BzNHCHCOOC}_2\text{H}_5$	69—71 70% EtOH	58	62.13	6.82	5.57	62.15	6.74	5.47
3	OC_3H_7 $\text{BzNHCHCOOC}_3\text{H}_7$	54—55 70% EtOH	41	64.51	7.57		64.70	7.52	
4	$\text{OC}_{11}\text{H}_{23}$ $\text{BzNHCHCOOC}_{11}\text{H}_{23}$	52—53 MeOH	50	74.50	10.80		74.55	10.60	
5	$\text{OCH}(\text{CH}_3)_2$ $\text{BzNHCHCOOCH}(\text{CH}_3)_2$	80—81 70% MeOH	44	64.51	7.57		64.30	7.49	
6	$\text{OC}(\text{CH}_3)_3$ $\text{BzNHCHCOOC}(\text{CH}_3)_3$	135—137 MeOH	23	66.41	8.19	4.55	66.33	8.32	4.64
7	$\text{OCH}_2\text{C}_6\text{H}_5$ $\text{BzNHCHCOOCH}_2\text{C}_6\text{H}_5$	95—96 EtOH	52	73.60	5.60		73.60	5.50	
8	OC_6H_{11} $\text{BzNHCHCOOC}_6\text{H}_{11}$	118—119 MeOH	53	70.16	8.12		70.20	8.19	
9	OH $\text{BzNHCHCOOC}_6\text{H}_5$	159—160 MeOH	29	66.42	4.83		66.71	4.85	
10	OCH_3 $\text{BzNHC}(\text{CH}_3)\text{COOCH}_3$	114—115 MeOH + Et_2O	29	60.50	6.32		60.60	6.36	
11	$\text{OC}(\text{CH}_3)_3$ $\text{BzNHC}(\text{CH}_3)\text{COOH} \cdot \text{H}_2\text{O}$	103—104 70% EtOH	48	58.00	7.11		58.34	7.08	
12	$\text{OCH}_2\text{C}_6\text{H}_5$ BzNHCHCOOH	123—125 70% EtOH	7	67.35	5.30	4.00	67.23	5.45	4.89
13	OH $\text{BzNHCHCOOCH}_2\text{C}_6\text{H}_5$	125—126 70% EtOH	31	67.35	5.30	4.00	67.20	5.31	4.93
14	OCH_3 $\text{BzNHCHCOOC}(\text{CH}_3)_3$	125—126 70% MeOH	39	62.15	6.81		62.27	6.86	
15	NHC_6H_5 $\text{BzNHCHCOOCH}_2\text{C}_6\text{H}_5$	150—157 MeOH	29	73.31	5.59	7.76	72.70	5.21	7.65
16	NC_6H_5 $\text{BzNHCHCOOCH}_2\text{C}_6\text{H}_5$	76—79 70% MeOH	3			7.94			8.00
17	NHC_6H_5 $\text{BzNHCHCOOC}(\text{CH}_3)_3$	155—156 MeOH	68	69.93	6.77	8.62	69.90	6.71	8.63
18	NHC_6H_5 $\text{BzNHCHCONHC}_6\text{H}_5$	163—164 MeOH	70	73.04	5.50	12.17	72.97	5.53	11.95
19	$\text{SCH}_2\text{C}_6\text{H}_5$ $\text{BzNHCHCOSCH}_2\text{C}_6\text{H}_5$	103—104 MeOH	77	67.78	5.17		68.08	4.85	

*The yields were calculated on half the quantity of initial oxazolinone, since the second half of the latter was converted into hydrobromide and was not subjected to bromination[1].

4. Preparation of Compound 9 was carried out under the conditions of Experiment 1 using 2.9 g of freshly distilled phenol. The reaction mixture was washed twice with water, more water was added, and it was left for a day, after which the precipitate was filtered off.

5. Preparation of Compound 12. To a solution of 4-bromo-2-phenyloxazolinone-5 prepared under the conditions of Experiment 1, was added, at 0°, a mixture of 0.27 g of water and 6 ml of dioxane, the solution was stirred at 0° for 0.5 hour, 3.4 g of benzyl alcohol was added, and the stirring was continued at 20° for 1.5 hours. The reaction mixture was then washed with water, dried over Na_2SO_4 , evaporated in a vacuum, and the residue ground in an 8% solution of NaHCO_3 . Upon acidification of the solution thus obtained, a precipitate formed which was filtered.

6. Preparation of Compound 13. To a dichloroethane solution of 4-bromo-2-phenyloxazolinone-5 at 0°, prepared as in Experiment 1, was added 1.7 g of benzyl alcohol, and the mixture was stirred for 1 hour at 0°. The reaction mixture was then washed with water, dried over Na_2SO_4 , evaporated under vacuum, and the residue ground with ether and filtered.

7. Preparation of compounds 15 and 16. To a dichloroethane solution of 4-bromo-2-phenyloxazolinone-5 at 0°, prepared as in Experiment 1, was added 1.7 g of benzyl alcohol; the mixture was stirred at this same temperature for 20 minutes, and 3 g of aniline was then added. After 2 hours, the precipitate of Compound 15 was filtered and washed free of aniline hydrobromide with water. If 3.5 g of piperidine is used in place of aniline, Compound 16 is obtained.

8. Preparation of Compound 17 was carried out under the conditions of Experiment 1 using 6 g of absolute trimethylcarbinol. After stirring the reaction mixture for 1 hour, 5 g of aniline was added; after 15 minutes, the precipitated aniline hydrobromide was filtered off, and the solution was washed with 5% HCl and water, dried over Na_2SO_4 , and evaporated under vacuum.

9. Preparation of Compound 18 was carried out under the conditions of Experiment 1 using, in place of the alcohol, 10 g of aniline which was added at -5 to 0°. The temperature was slowly raised to 25°, and the mixture was stirred for 1 hour, after which the precipitated aniline hydrobromide was filtered off, the solution washed with 5% HCl and water, dried over Na_2SO_4 , and evaporated under vacuum.

10. Preparation of Compound 19 was carried out under the conditions of Experiment 1 using 6 g of carefully dried benzyl mercaptan in place of the alcohol.

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THE INFLUENCE OF TEMPERATURE ON THE WEAKENING OF METAL ALLOYS

I.I. Kornilov

(Presented by Academician I.P. Bardin on July 23, 1955)

In studying the relationship between the weakening of metals and alloys and the temperature it is necessary to distinguish between the loss in strength of the pure metals and of the metal alloys when they are heated to high temperatures.

The strength of pure metals is a constant value, inherent to the given element. It can be changed within certain limits depending on the degree of purity of the metals. The temperature of weakening, for the pure metals, according to A.A. Bochvar, corresponding to the recrystallization temperature, is well-known [1]; it is equal to 0.3-0.4 of the absolute melting point ($T_{m.p.}$).

Even though the dependence of the strength of metal alloys on the temperature is associated with the strength of the pure metal, still it suffers changes and lends itself to regulation. These changes can be achieved first of all on the basis of changing the chemical composition and structure of the alloys. An increase in this strengthened condition to 0.5-0.6 $T_{m.p.}$ was shown for metal alloys by A.A. Bochvar [2]. At temperatures above 0.6 $T_{m.p.}$ the strengthening that results from solid solution alloying drops sharply. In this study the above author admitted some possibility of alloy strengthening at even higher temperatures if the compositions of the separated phases and solid solutions are made more complex.

The large wealth of theoretical and experimental material accumulated in studying the heat-resistance of metal alloys as a function of chemical structure and temperature [3-6] makes it possible to define and calculate the threshold temperatures, at which the strengthened condition of alloys is retained, and to compare them with the weakening temperatures of the pure metals.

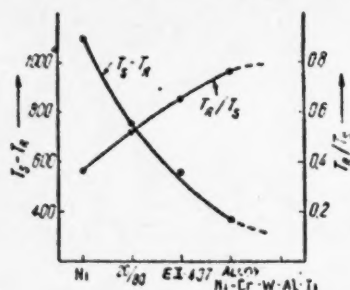
Earlier it was established that under the sharp strength reduction shown by such metals as iron and nickel at high temperatures (700-900°), in contrast the alloys prepared on their base show considerable strengthening at these temperatures [6]. Here the strengthened state at high temperatures is retained the longer the more complex the compositions of the solid solutions - the bases and the excess phase, separating here in the finely-dispersed state.

As a result, in a series of metal systems the threshold temperature of the strengthened state increases in a stepwise manner from binary to ternary to quaternary and more complex systems. We will conditionally take the strength endurance temperature $\sigma_{100 hrs} = 15 \text{ kg/mm}^2$ as the temperature at which the strengthened state is retained, for example, for nickel alloys at high temperatures. Then it can be shown which alloys, and at what temperatures (in percents to the absolute melting points), retain such strength endurance.

These values for nickel and its alloys are given in Table 1. Also given in the table are the melting point data, the maximum temperature at which the strength endurance limit $\sigma_{100 hrs} = 15 \text{ kg/mm}^2$ is retained, and the ratio of the absolute temperature of the strengthened state to the absolute melting point of the nickel alloys. This information is given for pure nickel, the binary Ni-Cr alloy with 20% chromium (nichrome type), the ternary Ni-Cr-Ti alloy with 20% Cr and 2.5% Ti (EI-437 type [7]), and the experimental quinary Ni-Cr-W-Ti-Al alloy having the composition 20% Cr, 6% W, 20% Ti, 4.5% Al.

The curves for nickel and its alloys are shown in Fig. 1, one of which (T_R/T_S) shows the increase in the ratio of the threshold temperature for $\sigma_{100 hrs} = 15 \text{ kg/mm}^2$ to the absolute melting point of the metal or alloy, while the other ($T_S - T_R$) shows the difference between the melting point and the maximum heat-resistance

threshold temperature. These curves clearly show that in measure with increase in the complexity of the base solid solutions that a considerable increase in the threshold temperature of the strengthened state of the alloys is shown. This produces a reduction in the difference between the melting point of the alloys and the threshold temperature at which the strengthened state of the alloys is retained. As a result, in measure with complexity increase in the chemical composition the melting points of the alloys go down, and the temperatures of the strengthened states go up. This finds expression in the gradual rise of the temperature of the strengthened state with respect to the absolute melting point of the alloys. This value rises from 0.4 $T_{m.p.}$ for pure nickel to 0.50 $T_{m.p.}$ for the binary nichrome alloy, to 0.65 $T_{m.p.}$ for the EI-437 alloy, and to 0.75 $T_{m.p.}$ for the experimental quinary Ni-Cr-W-Ti-Al alloy of the given composition. However, the course of the curve shows that the increase in these values becomes slower as the melting points are approached. It can be seen that the limiting value for the alloys of highest complexity will be 0.75-0.80 $T_{m.p.}$



Nickel and its Alloys

Fig. 1. Change in the ratio T_R/T_S and difference $T_S - T_R$ in nickel alloys.

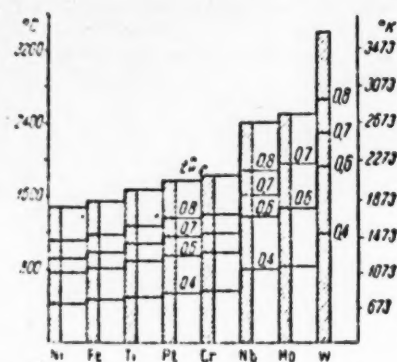


Fig. 2. Melting points of some metals and the calculated 0.4, 0.6, 0.7 and 0.8 portions of their melting points.

those potential possibilities that are concealed by these metals for the creation of new heat-resistant alloys on their base. In Fig. 2 are plotted the melting points (in $^{\circ}\text{C}$ and $^{\circ}\text{K}$) and the values, corresponding to 0.4, 0.6, 0.7 and 0.8 of the absolute melting points of the pure metals, for: nickel, iron, titanium, platinum, chromium, niobium, molybdenum and tungsten.

As a rule, the melting points of the alloys based on these metals (and correspondingly the 0.4, 0.6, 0.7 and 0.8 portions of these temperatures) will be lower than for the pure metals.

Even assuming, for example, a value of 0.6 $T_{m.p.}$ of the pure metals as a basis for calculating the threshold temperatures of the strengthened state of alloys, it becomes possible to achieve the following threshold temper-

Consequently, by judicious alloying, making more complex the chemical composition of the base solid solutions, and creating conditions for retaining the disperse separation of excess phase from the complex composition of solid solutions, it becomes possible to raise the temperature limits of the strengthened state of alloys to 0.80 of the absolute melting points possessed by the alloys.

This permits raising, for example, the temperature limits of the strengthened state for nickel alloys of complex chemical composition up to a temperature of nearly 1000 $^{\circ}$.

If the propositions demonstrated on the example of nickel and its alloys regarding the threshold temperatures for retention of the strengthened state are correct, then it can be assumed that they should also be operative to some degree for other alloys that are based on high-melting metals.

In examining this problem a distinction should be made between the heat-resistance shown by alloys based on metals that crystallize with a face-centered lattice (Fe, Co, Ni, Pt, etc.), those that crystallize with a body-centered lattice (Fe, Cr, V, Mo, etc.), and those with a hexagonal lattice (Mg, Ti, Zr, etc.).

As can be shown on the example of iron, with other conditions constant the ferrite alloys with a body-centered lattice are less heat-resistant than the austenite alloys with a face-centered lattice. It can also be established on the examples of magnesium and titanium that the metals with a hexagonal lattice show lower heat-resistance than do the metals with a face-centered lattice, for example aluminum and nickel.

An examination of this problem on the examples of other high-melting metals with a different type of crystal lattice is of great interest from the viewpoint of elucidating

atures for the heat-resistant alloys based on the metals: titanium 880°, chromium 970°, niobium 1346°, and molybdenum 1466°C. At 0.65 $T_{m.p.}$, these values rise even more, and specifically: for titanium to approximately 950°, for chromium to 1060°, for niobium to 1450°, and for molybdenum up to 1600°C.

In this connection it should be remembered that the alloys based on niobium and molybdenum are strongly oxidized at these temperatures and require special protective covers.

TABLE 1

Nickel and its alloys	Ni	Ni-Cr with 20% Cr	Ni-Cr-Ti EI-437 20% Cr 2.5% Ti	Experimental Ni-Cr-W-Ti-Al alloy 20% Cr, 6% W 2% Ti, 4.5% Al
M.p. in °C (°K)	1455 (1728)	1400 (1673)	1380 (1653)	1360 (1633)
Maximum temperature for $\sigma_{100hrs} = 15 \text{ kg mm}^2$ in °C (°K)	~418 (691)	600 (873)	800 (1073)	950 (1223)
Ratio of the maximum tem- perature of the strengthened state to the m.p. of the alloy	~0.40	~0.50	~0.65	~0.75

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MOBILITY OF SULFUR IN ORGANOTHIOPHOSPHORUS COMPOUNDS

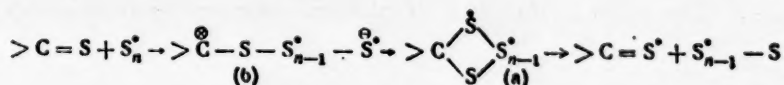
TRIALKYLTHIONOPHOSPHATES AND DIALKYLDITHIOPHOSPHATES

G.P. Miklukhin, L.V. Sulima, T.A. Mastryukova and Acad. Sci. USSR

Corresponding Member M.I. Kabachnik

In previous studies it was shown that in organic compounds the sulfur, entering into the composition of the groupings C-SH and C-S-C, fails to exchange either with elementary sulfur [1-5] or with the sulfur of hydrogen sulfide [6]. In contrast to this, the sulfur of the thiono groupings [1-5], and especially the sulfur of the dithio acids [2, 7, 8], shows great mobility and exchanges with elementary sulfur under conditions that become milder the more negative the charge on the sulfur in the C=S group.

It was postulated [1, 2, 7, 8] that the examined exchange reactions proceed through the (a) type of intermediate compounds, the formation of which becomes possible for the reason that the S-S bonds in cyclic sulfur molecules are easily polarized and suffer heterolytic cleavage when reacted with the negatively polarized sulfur group $\overset{\delta+}{C} = \overset{\delta-}{S}$.



The ability shown by sulfur to give multiple chains is well known. To realize the exchange reaction it is necessary to not only form chain compounds, but also to close the ring. In this connection, the cleavage of both radioactive and nonradioactive sulfur becomes equally probable.

To obtain some new data on the structure and reactions of the full and acid esters of the mono- and dithiophosphorus acids and their salts of general type $(RO)_3PS$; $(RO)_2PS(SR)$; $(RO)_2PSSH$; $(RO)_2PSOH$ [9-11], and also to verify the above-examined postulation, we studied the exchange reactions of the indicated compounds with sulfur.

As is shown by the results, given in Table 1, of our experiments on the exchange reaction of various mono- and dithiophosphorus acid derivatives with radioactive sulfur, in not a single case were we able to obtain an exchange, even though the experiments were run under quite drastic conditions, being close to the decomposition point of the studied compounds.

By way of comparison it should be mentioned that potassium ethylxanthate, containing, as it were, a similar dithio acid grouping of the atoms C_2H_5OCSSK exchanges two sulfur atoms even at 0° [7], while sodium diethyldithiocarbamate, $(C_2H_5)_2NCSSNa$, enters into rapid exchange reaction at 50-60° [2, 8].

What is the reason for such a sharp difference in the exchange capacity shown by the sulfur in carbon and phosphorus compounds of related structure? If the above given scheme holds true for the carbon compounds, then it could be assumed that its first stage should also be easily realized for the phosphorus compounds:

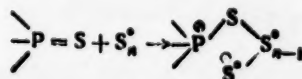


TABLE 1

Exp. Nos.	Exchanging substance	Wt. in g		Time in hrs	Temp in °C	Activity of the benzidine sulfate obtained from:		
		substance	S*			substance isolated from the mixture	sulfur isolated from the mixture	starting sulfur

Exchange for esters (solvent 1 ml of toluene)

1	$(C_2H_5O)_2P \begin{array}{l} \diagup S \\ \diagdown S-C_2H_5 \end{array}$	0.387	0.064	12	130	16	1470	1460
2	$(i-C_4H_9O)_2P=S$	0.304	0.064	12	130	11	1460	1460
3	$(i-C_4H_9O)_2P=S$	0.321	0.064	12	130	0	1460	1460
4	$(C_2H_5O)_2P \begin{array}{l} \diagup S \\ \diagdown S-CH_2CH_2SC_2H_5 \end{array}$	0.296	0.064	12	130	0	1470	1460

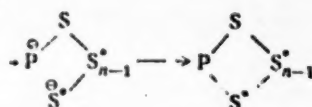
Exchange for salts and acids (solvent 2 ml of ethyl alcohol and 6 ml of benzene)

5	$(C_2H_5O)_2PS(SK)$	0.449	0.064	13	50	0	—	1730
6	$(C_2H_5O)_2PS(SK)$	0.446	0.064	6	85	0	1700	1720
7	$(C_2H_5O)_2PS(SK)$	0.446	0.064	18	100	0	—	1720
8	$(C_2H_5O)_2PS(SH)$	0.374	0.064	13	50	0	—	1730
9	$(C_2H_5O)_2PS(SH)$	0.372	0.064	6	85	0	1700	1720

As regards the second stage, then in the carbon series it corresponds to the formation of substances of the type of mercaptals or of the orthoesters of trithio acids. In phosphorus compounds the substances containing the

$\begin{array}{c} SR \\ | \\ P \\ | \\ SR \end{array}$ grouping are unknown and, it must be assumed, should be extremely unstable. In general, pentavalent

phosphorus compounds are rarely formed. The following types of compounds are more or less stable: PF_5 , $P(C_6H_5)_5$ [12], $P(OC_6H_5)_5$ [13]. Pentavalent phosphorus compounds containing alkyl radicals are extremely unstable. Apparently the realization of the stage,



which could lead to exchange, is thermodynamically impossible for this reason, and this explains the results obtained by us, testifying to the absence of sulfur exchange in the examined organophosphorus compounds.

Exchange Experiments with Radioactive Sulfur (Table 1).

To determine the activity of the exchanged components they were subjected after separation to Curium combustion. The sulfate obtained here was converted into benzidine sulfate, in 4 mg specimens of which was determined the activity in impulses per minute after subtracting the ground.

The exchange experiments were run in sealed glass ampuls, which were heated for a definite time at a predetermined temperature. After being heated the ampul was opened and the substances subjected to exchange were separated. For this in all cases the solvent was removed by evaporation at room temperature in a stream of air, after which ethyl alcohol was added to the residue. Here the substance dissolved, while the sulfur separated out as crystals, which were filtered and air-dried.

In the case of exchange with the salts the alcohol solution was again evaporated, the residue was dissolved in water, and the solution was filtered and then evaporated on the water bath. In the case of exchange with the

acids the alcohol solution was treated with KOH until slightly acid, the solution was filtered and evaporated on the water bath, and the dry residue was washed by decantation with ether (to remove the acid). The melting point of the isolated salt, both in the case of salt exchange and that obtained from the acids, varied in the limits 182-184° (the melting point of the starting salt was 183-184°).

In the case of exchange with the esters the alcohol was vacuum-distilled from the solution at room temperature. The ester remaining was freed from dissolved sulfur by high vacuum-distillation under heating. Here the sulfur deposited on the sides of the distillation flask, while the ester passed into the receiver. As can be seen from Expts. 1 and 2, in some cases we were not always able to obtain complete separation. The degree of purity of the ester isolated after exchange was determined from its index of refraction. The index of refraction values obtained for the esters are given in Table 2.

TABLE 2

Exp. Nos.	Substance	n_D^{20}	
		in the starting substance	in the isolated substance
1	$(C_2H_5O)_2PS(SC_2H_5)$	1.5013	1.500
2	$(i-C_4H_9O)_3P = S$	1.4443	1.450
3	$(i-C_5H_{11}O)_3P = S$	1.4500	1.452
4	$(C_2H_5O)_2P \begin{matrix} \nearrow S \\ \searrow S-CH_2CH_2SC_2H_5 \end{matrix}$	1.5341	1.532

In the experiments run at 140-150° there occurred considerable decomposition of both the salts and the acids, and we were unable to isolate them in the pure form. The substances, soluble in alcohol, were precipitated with silver nitrate. The obtained precipitate failed to melt up to 150°, although the silver salt $(C_2H_5O)_2PSSAg$ melts at 94.5-95.5°. After Carius combustion the indicated precipitates gave a benzidine sulfate with an activity of 9 and 59 imp./min. in the salt exchange (at 140° for 8 and 30 hours, respectively), and 37 imp./min. in the exchange with the acids (at 140° for 30 hours). Considering that the starting sulfur had an activity of 1370 imp./min. it must be assumed that the sulfur in the mentioned products is inactive. At the same

time the activity of the sulfur, isolated from the reaction mixture, is considerably below that of the starting sulfur. This should be explained as being due to its dilution by the sulfur that is evolved in the decomposition of either the acid or the salt.

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CHEMICAL ISOLATION AND ANALYSIS OF METALLIC COMPOUNDS FORMED IN CERTAIN NICKEL ALLOYS

R.B. Golubtsova and L.A. Mashkovich

(Presented by Academician I.P. Bardin, August 9, 1955)

A knowledge of the composition and structure of metallic compounds arising in alloys is important in determining the reactions of metals. In a series of alloys, one and the same compound plays a dual role, strengthening or weakening depending on their composition, structure, and the degree of equilibrium.

The author of the first work dealing with intermetallide or phase analysis was Academician N.S. Kurnakov, who published in 1899, a work on the mutual compounds of metals [1]. In this work, he first described octahedral crystals of the compound NaCd_2 from alloys of the system sodium - cadmium. Ideally, intermetallide analysis, and also carbide analysis, is closely connected with the creation of new alloys [2-6].

In connection with the investigation of the state diagrams of simple and complex metallic systems [3,7], there has been great interest in the investigation of the question of the chemical isolation and study of metallic compounds which are formed, particularly in certain nickel systems. Taylor and Floyd [8] investigated the state diagram of the binary system nickel-titanium, and established the presence of the compound Ni_3Ti with a clear maximum in the curve and having a melting point of 1370° . The compound has a hexagonal lattice. In the literature on intermetallide analysis, the anodic liberation of an Ni_3Ti phase in iron-nickel-chromium alloys with titanium [2] and in nickel alloys [4] has been indicated. However, there has been no information in the literature on the possibility of the isolation of an Ni_3Ti phase in binary alloys by the method of intermetallide analysis.

TABLE 1

Results of the Analysis of Anodic Powders of the Binary System Ni-Ti. Duration of the experiment was 20 hours. Current density, 0.2 amps./sq cm.

Electrolyte No.	Weight of material collected g	Found, wt. %		Total, wt %	Ratio Ni:Ti, wt %	Found, atomic %		Total, atomic %	Atom ratio Ni:Ti, at. %	Structure of the phase isolated and its parameter*
		Ni	Ti			Ni	Ti			
Alloy with 7.91% Ti										
1	0.0226	74.78	20.31	95.09	3.80	76.02	23.99	99.11	3.20	Phase with face-centered cubic lattice, $a = 3.581$ on X
2	0.0462	78.60	21.60	100.10	3.66	74.89	25.11	100.00	2.68	
3	0.0053	77.73	21.67	99.40	3.59	75.54	24.90	100.44	2.93	
Alloy with 10.8% Ti										
1	0.0028	73.10	21.08	100.18	3.60	75.41	24.59	100.00	2.04	Ni ₃ Ti and a phase with a face-centered cubic lattice, $a = 3.581$ on X
Alloy with 12.94% Ti										
1	0.0408	78.05	21.20	99.25	3.68	75.00	25.00	100.00	3.00	Ditto
2	0.0228	77.05	20.90	98.85	3.72	75.27	24.69	99.96	3.04	
4	0.0193	78.80	21.20	100.00	3.71	75.21	24.79	100.00	3.03	

*The x-ray structural analyses presented in Tables 1, 2, and 3 were carried out at the metal-for-air-transport bench of the Zhukov A.Ya. Snetkov Military-Air Engineering Academy.

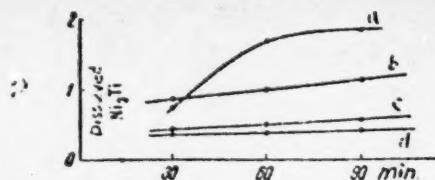


Fig. 1. Solubility of Ni_3Ti in mixtures of acids and methanol, a) 1% HCl + methanol; b) 1% H_2SO_4 + methanol; c) 1% HNO_3 + methanol; d) 1% HClO_4 + methanol.

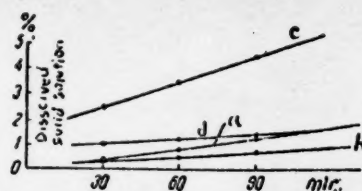


Fig. 2. Solubility of the solid solution in mixtures of acids and methanol, a) 1% HCl + methanol; b) 1% H_2SO_4 + methanol; c) 1% HNO_3 + methanol; d) 1% HClO_4 + methanol.

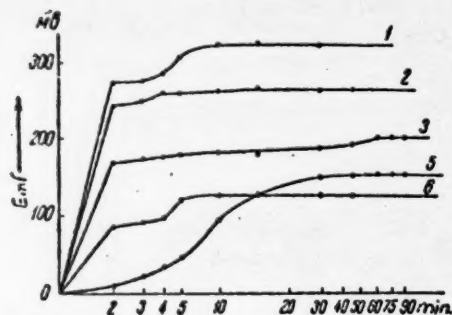


Fig. 3. Change in potential difference of the pair Ni_3Ti and nickel solid solution (with 5% Ti) with time in various electrolytes.

A study of the conditions for isolating the above-mentioned phase in nickel alloys entered into the problem of the present investigation. There were investigated:

1) Binary nickel-titanium alloys having titanium contents of 7.94, 10.8, and 12.94%. The alloys of this system were studied in the tempered state: 24 hours at 1150° , cooled to 800° and soaked for 100 hours, then cooled in a furnace.

2) The ternary alloy Cr 18.92%, Ti 8.38%, remainder nickel. Thermal treatment (tempering) regime of these alloys: 6 hours at 1200° , 18 hours at 1150° , 24 hours at 800° , cooling in air.

The alloy EI-437: Cr 20.5%, Si 0.35%, Ti 2.52%, Al 0.67%, remainder Ni. Tempering of this last alloy was carried out at 800° for a period of from 250 to 2000 hours.*

The samples of alloys for the investigation were prepared in the form of cylinders 40 mm high and 15 mm in diameter.

In the basic phase of the investigation, the optimum composition of electrolyte, which permitted isolation of the desired phase and which guaranteed its preservation during the electrolysis, was determined. Moreover, the chosen electrolyte had to promote maximum solution of the solid solution. With a view to the proper selection of electrolyte composition, for anodic solution, it was convenient to study the solubility of phases of stoichiometric composition for Ni_3Ti and the binary solid solution (with 5% Ti) in various chemical media.

Curves of solubility in these electrolytes were constructed from the data (see Figures 1 and 2). As seen from the results, the requirements were best satisfied by a mixture of 1% nitric acid in methanol. This mixture easily dissolved the nickel solid solution, while solution of the Ni_3Ti phase was very insignificant. Therefore,

*All alloys were prepared by L.I. Pryakhina in connection with an investigation of the properties, including the heat resistance, and state diagrams for these systems.

In all of the electrolytes (Nos. 1, 2, 3, and 4) we introduced 1% nitric acid. Further experiments on the solution of the Ni_3Ti phase and of the nickel solid solution (with 5% Ti) were carried out both in electrolytes recommended by us and in electrolytes used by other authors [4]. The duration of anodic solution was 7 hours.

Electrolyte No. 1 15 ml of HNO_3 (sp. gr. 1.40), 35 g citric acid, 5 g ammonium sulfate, 900 ml methanol, and 100 ml water.

Electrolyte No. 2 15 ml HNO_3 (sp. gr. 1.40), 35 g citric acid, 5 g ammonium sulfate, 1000 ml water.

Electrolyte No. 3 15 ml HNO_3 (sp. gr. 1.40), 25 g tartaric acid, 5 g ammonium sulfate, 1000 ml water.

Electrolyte No. 4 25 g tartaric acid, 15 ml HNO_3 , 5 g ammonium sulfate, 900 ml methanol, 100 ml water.

Electrolyte No. 5 10 g ammonium sulfate, 10 g citric acid, and 1200 ml water*.

Electrolyte No. 6 15 ml H_2SO_4 (sp. gr. 1.84), 35 g citric acid, 5 g ammonium sulfate, 900 ml methanol, and 100 ml water*.

As shown by our experiments, anodic deposits did not separate out in electrolytes Nos. 5 and 6 in the case of binary alloys.

Simultaneously with the selection of electrolyte compositions, we carried out experiments on the measurement of potential differences of the pair Ni_3Ti and the nickel solid solution (with 5% Ti). The measurement was carried out on a Type P-4 potentiometer, by the compensation method of Pogendorf, at the moment of immersion of the pair of electrodes and then through a specified time interval. The measurement was discontinued after stabilization of the potential difference reading in each electrolyte. On the basis of these experiments, curves showing the variation of emf (potential difference) with time were constructed, (see Figure 3).

The results of the measurements of potential differences agree well with data on the solubility of Ni_3Ti and the nickel solid solution (with 5% Ti) in the various solvents. The results of the experiments were used to establish the optimum compositions of the electrolytes for the isolation of metallic compounds in the alloys.

The anodic residues obtained after electrochemical solution of the alloy samples were centrifuged. The residue was dried in a stream of hydrogen; part was selected for X-ray analysis, and another part was first weighed on an analytical balance and then dissolved in a mixture of hydrochloric and nitric acids in a 100-ml beaker. After solution of the weighed sample, the solution was evaporated with sulfuric acid. The salts were dissolved in distilled water and transferred to a volumetric flask. Quantitative chemical analysis was carried out on aliquot portions of the solution. The results of the chemical analyses and the data from x-ray analyses of the isolated powders are presented in Tables 1, 2, and 3.

As seen from the experimental data presented in the tables, the isolation of an Ni_3Ti phase occurred in the various electrolytes containing nitric acid. The ratio of nickel to titanium in each of the anodic powders (in the binary and ternary alloys), both in weight and in atomic per cent,

*These electrolytes were prepared by N.I. Blok and co-workers [4].

**And traces of solid solutions.

TABLE 2
Results of Analyses of the Anodic Powders of Ternary Alloys of the System Ni-Cr-Ti. Duration of experiment, 3 hours. Current density 0.075 amp./sq. cm.

Electrolytic No.	Weight of powder collected, g	Found, weight %				Total weight %	Ni:Ti ratio	Found, atomic %			Total, atomic %	Ni:Ti ratio	Structure of the isolated phase
		Found, weight %			Mn								
		Ni	Ti	Cr				Ni	Ti	Cr			
1	0.0340	76.47	26.41	1.80	100.68	3.76	72.53	23.54	1.90	100.10	3.07	Ni ₃ Ti	
2	0.1000	73.42	21.84	1.83	99.32	3.76	72.43	23.40	2.00	99.95	3.09	Ni ₃ Ti	
3	0.0366	73.26	21.61	1.77	100.01	3.50	71.54	25.13	1.99	100.00	2.84	Ni ₃ Ti	
4	0.0473	73.85	19.36	1.94	96.17	3.56	73.01	22.22	2.10	99.40	3.28	Ni ₃ Ti	
5	0.0232	73.00	19.09	0.91	99.48	4.00	75.24	22.20	0.97	99.88	3.38	Ni ₃ Ti and traces of solid solution	

TABLE 3

Results of Analyses of Anodic Powders from EI-437 Alloy After Aging at 800°. Duration of the experiments, 7 hours. Current density, 0.075 amps./sq. cm.

Time of aging, hours	Electrolyte No.	Yield of powder, weight % of the dissolved portion of anode	Found, weight %				Total, weight %	Structure of the isolated phase
			Ni	Ti	Cr	Al		
250	6	3.1	70.04	14.00	5.30	11.21	100.55	Phase with face-centered cubic lattice, $a = 3.581$ on X
	1	3.2	78.70	11.01	3.00	10.00	100.80	
500	6	3.6	73.88	11.30	4.74	9.80	99.70	
	1	4.1	73.38	11.00	2.49	14.61	101.29	
750	1	4.9	68.38	12.84	4.09	14.28	99.57	
1000	6	7.0	76.34	12.65	6.02	3.63	99.58	
1250	6	8.0	76.00	12.50	6.85	3.69	99.04	
	1	8.3	71.60	12.40	8.00	6.32	100.32	
2000	6	9.2	75.87	12.40	6.30	5.53	100.10	

corresponded to theoretical. The theoretical ratios from the formula Ni_3Ti are $Ni:Ti = 3.67$ weight per cent and $Ni:Ti = 3$ atomic per cent. X-ray analysis established that the isolated phase has a hexagonal lattice. An α -phase was found in the EI-437 alloy with different aging times, which confirms the work of N.I. Blok and co-workers [4].

The experiments carried out to study the conditions for solubility of the metallic compound Ni_3Ti and the nickel solid solution (with 5% Ti) in different chemical media, and also the experiments on the measurement of potential differences, confirm that the best electrolytes, which guarantee isolation of the Ni_3Ti phase, are electrolytes containing nitric acid. These electrolytes isolate from the binary Ni-Ti and the Ni-Ti-Cr alloys a phase which has the composition Ni_3Ti .

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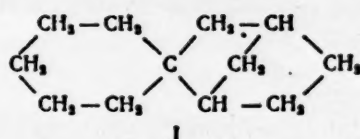
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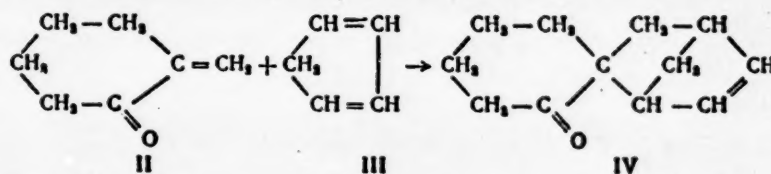
SYNTHESIS OF 1,4-ENDOMETHYLENESPIRO(5,5)UNDECANE

N.V. Elagina, V.M. Brusnikina and Academician B.A. Kazansky

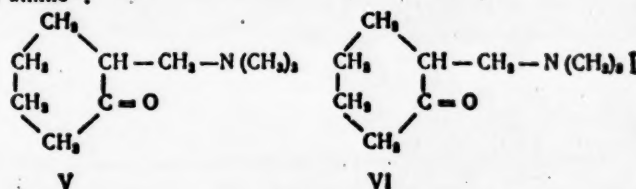
The objective of the present work was the synthesis of the tricyclic spirane hydrocarbon, 1,4-endomethylenespiro(5,5)undecane (I).



As a basis for the synthesis of this hydrocarbon, we chose the dienic reaction between 2-methylenecyclohexanone-1 (II) and cyclopentadiene (III), which leads to the formation of the unsaturated spiro ketone 1,4-endomethylenespiro(5,5)undecen-2-one-7 (IV).

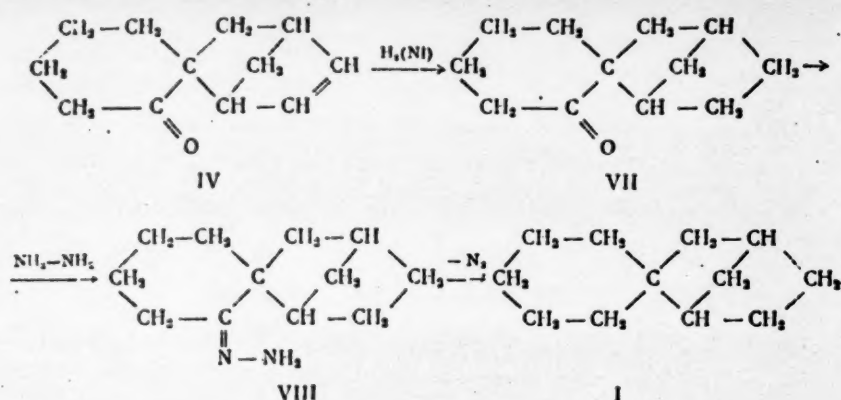


It is known from the literature [1, 2] that 2-methylenecyclohexanone-1 cannot be isolated in the free state owing to its great tendency toward polymerization. For the preparation of this ketone, we made use of 2-(N-dimethylaminomethyl)-cyclohexanone-1 (V) or its methiodide (VI), which decomposed under the conditions of the experiment with the formation of 2-methylenecyclohexanone-1 (II) and, respectively, the secondary amine or the salt of the tertiary amine*:



By heating 2-(N-dimethylaminomethyl)-cyclohexanone-1 (V) with cyclopentadiene we obtained 1,4-endomethylenespiro(5,5)undecen-2-one-7 (IV). We also prepared this ketone by heating the methiodide of 2-(N-dimethylaminomethyl)-cyclohexanone-1 (VI) with cyclopentadiene in an aqueous alcoholic medium. 1,4-Endomethylenespiro(5,5)undecanone-7 (VII) was prepared by the catalytic reduction of 1,4-endomethylenespiro(5,5)undecen-2-one-7 (IV) in the presence of Raney nickel. The ketone (VII) was converted by the action of hydrazine hydrate into the hydrazone (VIII), and the latter was subjected to catalytic decomposition in the presence of potassium hydroxide and platinized charcoal.

*The possibility of the reaction of 2-methylenecyclohexanone-1 obtained from 2-(N-dimethylaminomethyl)-cyclohexanone-1 with cyclopentadiene was indicated in a brief note by Jacquier and Christol [3].



The 1,4-endomethylenespiro(5,5)undecane prepared by us was a colorless, rather mobile liquid with a characteristic terpene odor and the following properties: b.p. 98° at 10 mm; n_D^{20} 1.4987; d_4^{20} 0.9468; M_R^D 50.92, calculated for $C_{12}H_{20}$ 51.01.

EXPERIMENTAL

2-(N-Dimethylaminomethyl)-cyclohexanone-1 was prepared from cyclohexanone, dimethylamine hydrochloride, and formaldehyde. B.p. 92° at 10.5 mm; n_D^{20} 1.4672; d_4^{20} 0.9504; M_R^D 45.34, calculated for $C_9H_{17}ON$ 45.51; yield 73.6% of theory.

Literature data [4]: b.p. 100° at 13 mm; [5]: b.p. 97-100° at 13 mm; [2]: b.p. 93-94° at 11.5 mm; [6]: b.p. 96-97° at 11.5 mm; [7]: b.p. 60° at 1 mm, n_D^{20} 1.4670.

Methiodide of 2-(N-dimethylaminomethyl)-cyclohexanone-1 was prepared by the action of methyl iodide, on 2-(N-dimethylaminomethyl)-cyclohexanone-1 in a medium of dry ether. M.p. 144-144.5° (after recrystallization from ethyl alcohol); yield 85.8% of theory.

Literature data: m.p. 136-137° [2]; m.p. 152-153° [6].

1,4-Endomethylenespiro(5,5)undecen-2-one-7 was prepared by the reaction of cyclopentadiene with the methiodide of 2-(N-dimethylaminomethyl)-cyclohexanone-1 (Experiment 1) and by the reaction of cyclopentadiene with 2-(N-dimethylaminomethyl)-cyclohexanone-1 (Experiment 2).

Experiment 1. In a 250-ml, three-necked, round bottom flask provided with an oil-sealed mechanical stirrer, a reflux condenser, and a dropping funnel were mixed 63.3 g (0.21 mole) of the methiodide of 2-(N-dimethylaminomethyl)-cyclohexanone-1, 60 ml of ethyl alcohol, 15 ml of water, and 0.5 g of hydroquinone. A solution of 21 g (0.32 mole) of cyclopentadiene in 10 ml of ethyl alcohol was added, with mixing, from the dropping funnel. The mixture was refluxed on a water bath with mixing for 8 hours, after which the alcohol was distilled off. 15 ml of water was added to the residue to dissolve the precipitated trimethylamine hydroiodide, and the upper, oil layer was separated. The water layer was extracted with ether, and the ethereal extract was combined with the previously separated oil. The ethereal solution was washed with water and dried with anhydrous magnesium sulfate. The ether was distilled off, and the residue was fractionated under vacuum. 9.7 g (25.9% of theory) of 1,4-endomethylenespiro(5,5)undecen-2-one-7 was obtained having the following constants: b.p. 107-107.5° at 4 mm; n_D^{20} 1.5154; d_4^{20} 1.0591; M_R^D 50.22, calculated for $C_{12}H_{18}C(F)$ 50.56.

Found %: C 82.15; 82.08; H 9.36; 9.36
 $C_{12}H_{18}O$. Calculated %: C 81.77; H 9.15

The ketone was a colorless, rather mobile liquid with the odor of menthol.

The semicarbazone of 1,4-endomethylenespiro(5,5)undecen-2-one-7 had an m.p. of 196-196.5° (after recrystallization from ethyl alcohol).

Found %: C 66.88; 66.79; H 8.33; 8.23; N 17.68; 17.84
 $C_{13}H_{19}ON_3$. Calculated %: C 66.92; H 8.21; N 18.02

The oxime of 1,4-endomethylenespiro(5,5)undecen-2-one-7 had an m.p. of 84.5-85° (after recrystallization from ethyl alcohol).

Found %: C 75.65; 75.68; H 9.13; 9.24; N 7.37; 7.47
 $C_{12}H_{17}ON$. Calculated %: C 75.35; H 8.96; N 7.32

Experiment 2. Into a 150-ml glass tube were introduced 46.6 g (0.3 mole) of 2-(N-dimethylaminomethyl)-cyclohexanone-1, 29.7 g (0.45 mole) of cyclopentadiene, and 1 g of hydroquinone. The tube was placed in an autoclave which was heated with agitation for 6 hours at 130°. After cooling the autoclave, the reaction mixture was dissolved in ether. The ethereal solution was washed with water, a 5% solution of hydrochloric acid, a 5% solution of soda, and once more with water, and dried with anhydrous magnesium sulfate. The ether was distilled off, and the residue was fractionated under vacuum. 19.1 g (36.1% of theory) of 1,4-endomethylenespiro(5,5)undecen-2-one-7 was obtained with these constants: b.p. 110-111° at 5 mm; n_D^{20} 1.5163; d_4^{20} 1.0585; MR_D 50.32, calculated for $C_{12}H_{18}O(F_2)$ 50.56.

1,4-Endomethylenespiro(5,5)undecanone-7. In a hydrogenation vessel were placed 17.21 g (0.098 mole) of 1,4-endomethylenespiro(5,5)undecen-2-one-7, 150 ml of ethyl alcohol, and 0.9 g of Raney nickel. 2205 ml (0°, 760 mm) of hydrogen was consumed over a period of 4 hours, 15 minutes, after which the hydrogenation rate dropped off sharply and the experiment was terminated. The catalyst was filtered off. After distillation of the alcohol, the ketone was dried with anhydrous magnesium sulfate and distilled under vacuum. 15.3 g (87.9% of theory) of 1,4-endomethylenespiro(5,5)undecanone-7 was obtained which had the following constants: b.p. 101-102° at 2 mm; n_D^{20} 1.5086; d_4^{20} 1.0442; MR_D 50.94, calculated for $C_{12}H_{20}O$ 51.02.

Found %: C 81.21; 81.25; H 10.17; 10.16
 $C_{12}H_{20}O$. Calculated %: C 80.85; H 10.18

The ketone was a colorless, thick liquid with the odor of menthol.

The semicarbazone of 1,4-endomethylenespiro(5,5)undecanone-7 had a m.p. of 194.5-195° (after recrystallization from ethyl alcohol).

Found %: C 66.40; 66.50; H 9.15; 9.17; N 17.81; 17.96
 $C_{13}H_{21}ON_3$. Calculated %: C 66.35; H 9.00; N 17.86

The oxime of 1,4-endomethylenespiro(5,5)undecanone-7 had an m.p. of 86-87° (after recrystallization from ethyl alcohol).

Found %: C 74.92; 74.93; H 10.01; 10.04 N 7.52; 7.61
 $C_{12}H_{19}ON$. Calculated %: C 74.56; H 9.9; N 7.25

1,4-Endomethylenespiro(5,5)undecane. 45.5 g (0.26 mole) of 1,4-endomethylenespiro(5,5)undecanone-7, 42.6 g (0.77 mole) of 90% hydrazine hydrate, and 70 ml of ethyl alcohol were placed in a 250-ml round bottom flask. A reflux condenser was joined to the flask which was then heated on an oil bath for 6 hours, the temperature being maintained at 120°. After this, the alcohol and the unreacted hydrazine hydrate were distilled off from the reaction mixture. The residue in the flask was dried with solid potassium hydroxide, and the supernatant hydrazone was separated from the water layer and dried with fused potassium hydroxide. 49 g of 1,4-endomethylenespiro(5,5)undecanone-7 hydrazone was obtained; this material was a thick, light yellow oil. The hydrazone was subjected to catalytic decomposition. In a 100-ml Wurtz flask, fitted with a thermometer and a downward-flowing condenser, were placed the 1,4-endomethylenespiro(5,5)undecanone-7 (49 g), 2 g of freshly fused potassium hydroxide, and 0.15 g of platinized charcoal. The mixture was heated on a metal bath, the temperature of which was slowly increased. A vigorous reaction set in at a bath temperature of 190°. The hydrocarbon was totally distilled at bath temperature of 250-280° and an effluent vapor temperature of 226-230°. The distillate was redistilled over fresh catalyst. The hydrocarbon obtained was washed with 50% acetic acid, then with water, a 3% solution of potassium hydroxide, and again with water, dried with fused potassium carbonate, and distilled under vacuum. 27 g (64.4% of theory) of 1,4-endomethylenespiro(5,5)undecane was obtained having the following constants: b.p. 98° at 10 mm; n_D^{20} 1.4987; d_4^{20} 0.9468; MR_D 50.92, calculated for $C_{12}H_{20}$ 51.01.

Found %: C 87.80; 87.66; H 12.21; 12.14
 $C_{12}H_{20}$. Calculated %: C 87.73; H 12.27

In another experiment, 25.6 g (62.9% of theory) of 1,4-endomethylenespiro(5,5)undecane was obtained from 44.2 g (0.25 mole) of 1,4-endomethylenespiro(5,5)undecanone-7.

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THE MECHANISM OF THE FORMATION OF AUSTENITE DURING FAST HEATING

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(Presented by Academician N.T. Gudtsov, August 9, 1955)

The mechanism of the formation of nuclei of austenite has not been subjected to direct experimental determination up to the present time. The study of this mechanism is difficult even during slow heating, and is still more difficult during fast heating. At the present time, there is no doubt that the architecture of the crystalline grains and, in particular, of the ferrite grains is complicated both as a consequence of exterior mechanical action (mechanical hardening) and as a result of volume changes arising during phase transformations (phase hardening). The change of the internal structure of the crystallites during plastic deformation has been studied in a series of native [1-6] and foreign [7-10 and others] investigations. The change observed in the properties of the metal during this has been interpreted as being the result of fragmentation of crystals and the emergence of additional deformations of the lattice of internal blocks.

The minute structure of the crystal was studied by G.V. Kurdyumov and L.I. Lysak [11] during the annealing of high-carbon steel and also in a series of investigations by L.S. Moroz [12-15] during the annealing of iron alloys which were subjected (before annealing) to tempering by the usual slow heating.

In Figure 1 is shown a microphotograph of the structure of technically pure iron; the photograph was made by A.I. Gardin [16] with an electron microscope at a magnification of 9000 diameters. The grain boundaries (in the lefthand part of the picture) are clearly marked by the lighter borders (in comparison with the blocks themselves).

It can be surmised that more carbon atoms than correspond to the limiting solubility in α -iron are included in the boundaries of the grains of the mosaic. The possible supersaturation of the boundaries by carbon, as shown by our experiments described in the present work, amounts to 0.25%. In such a case, the transformation into austenite in these spaces and under conditions of fast, continuous heating is stable not at 910°, as in the case of pure α -iron, but at 820°.

Upon the emergence of the first nuclei of austenite at the boundary between cementite and ferrite, diffusion movement of the austenite - ferrite boundary to the ferrite side begins. When a temperature of 820° is reached, there is generated a process of formation of austenite at the places where the boundaries which are moving by diffusion intersect with the boundaries of the blocks of the mosaic. Together with the diffusion of the boundaries of the austenite front (Figure 2a), a boundary complex of fine nuclei is formed (Figure 2b). The line of the austenite front, which is formed by this complex, intersects a considerably greater number of boundaries of neighboring blocks, and thus creates favorable conditions for the emergence of new austenite nuclei in still greater numbers for a further increase in the movement of the development front of the austenite (Figures 2c and 2d).

If this process is not stopped by an insufficient supply of energy, it develops at an increasing rate, and can capture the space between the neighboring perlite colonies before they could meet the diffusing boundaries of the first grains of austenite which grew. The space between the lines separating a potential position of the diffusing front of development of austenite grains from the neighboring perlite colonies (internal triangle mnp in Figure 2e) must be filled, by this process, with fine crystals of austenite in locales of former boundaries of blocks. The ferrite mosaic blocks are bordered by little chains of fine austenitic formations. Each nucleus of austenite, formed at the boundary of a block continues its development, on further heating, in all directions, capturing a certain part of the spaces of the adjoining blocks. This phenomenon is also accompanied by collective growth



Fig. 1. Microstructure of technically pure iron, $\times 9000$.

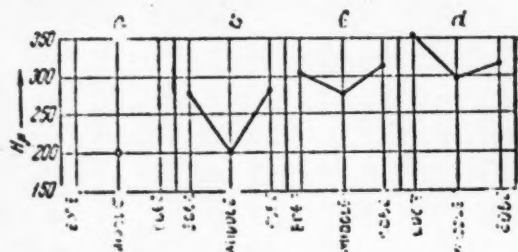


Fig. 3. Values of microhardness in the middle of a ferritic field of a steel with 0.24% C after tempering by heating at a rate of $V_{II} = 130^\circ/\text{second}$; a - tempering from 760° ; b - from 820° ; c - 840° ; d - 900° .

The transformation along the boundaries of the blocks in hypoeutectoidal carbon steel appears in the specific increase in hardness in the center of the ferrite grain after tempering at 820 - 840° , since, in this temperature interval, it is possible to assume an intensive progression of the transformation along the boundary.

In Figure 3 are presented the values of the microhardness (5-g load) at the edge and in the middle of the former ferritic field of a steel containing 0.24% C after heating at a rate of $V_{II} = 130^\circ/\text{second}$ to various temperatures and quenching in water. The values of the microhardness presented in Figure 3 are averages of values from measurements in 18-24 locales between the former perlite colonies. The increase in hardness in the middle of the ferrite zones on going from 820° to 840° (200 and 275 units, respectively) is clearly expressed. As our diffusion calculations showed, it is impossible to remove the increase in microhardness in the given case both on account of the diffusion process of austenite formation and on account of the creation of diamond pyramids of the ferrite surface, which is transformed as a result of the movement of the austenite boundaries toward the perlite zones. The increase in microhardness in the center of the ferritic space is observed only on quenching from a temperature of 840° , and this is explained, according to our ideas, by the change in the fine structure of the ferrite as a result of the transformation generated along the boundary of the blocks of the mosaic.

The existence of a transformation along the boundaries of the blocks of the mosaic was confirmed by an

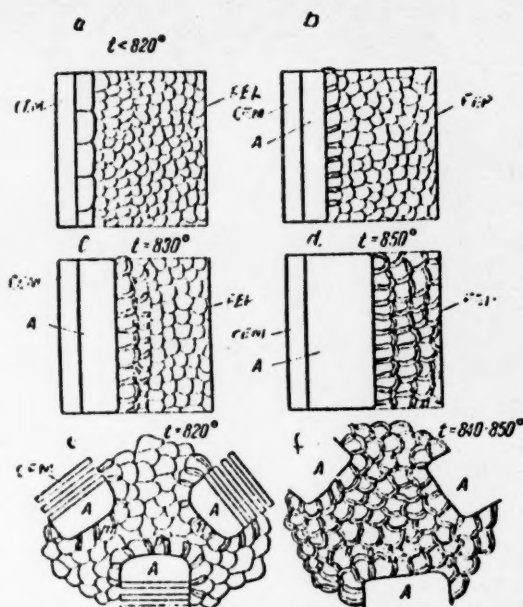


Fig. 2. Scheme of the development of the process of formation of austenite at the boundaries of blocks of the mosaic.

which unites into one grain several elementary boundary nuclei. At temperatures significantly above 820° , the development of the formation of austenite proceeds in the presence of a vast number of collisions of the elementary austenite front with the available austenite nuclei along the boundary of the blocks of the mosaic. At the moment of quenching, there can be created in the heated space a very granulated austenite having a multitude of the finest heterogeneities, as has been shown by us previously [17].

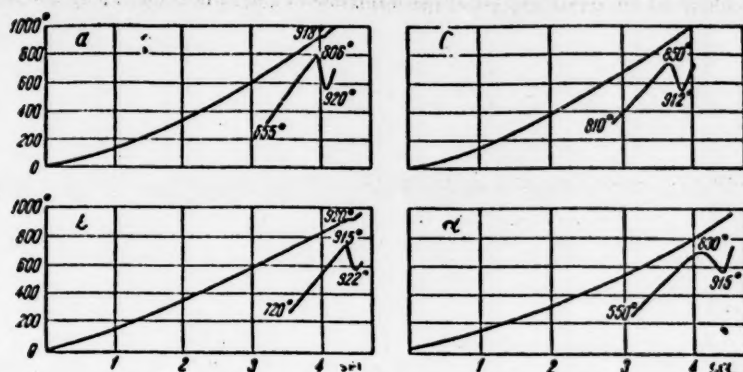


Fig. 4. Heating curves and dilatometric curves, a - for tempered technically pure iron containing 0.02% C, tempered at 960° for 2 hours, $V = 240^\circ/\text{second}$; b - for tempered technically pure iron with 0.07% C, tempered at 960° for 2 hours, $V = 200^\circ/\text{second}$; c - for quenched technically pure iron with 0.02% C, quenched from 960°, 5-minute soaking, $V = 250^\circ/\text{second}$; d - for quenched technically pure iron with 0.07% C, quenched from 960°, 5-minute soaking, $V = 200^\circ/\text{second}$.

investigation of contact electroheating of technically pure iron with simultaneous oscillographic recording of the thermal and dilatometric curves.

A capacitive dilatometer designed by A.V. Panov was used for the dilatometric investigation. Basically, this dilatometer works by comparing the frequencies of two strictly identical radio generators operating on a frequency of about 10 megacycles. Since both of these generators operated exactly alike, such factors as temperature of the surrounding medium, air pressure, and intensity of the field supply caused a change in the frequency of both generators in the same direction, and the difference in the frequencies changed insignificantly.

During a measurement, the capacity of the oscillating circuit was changed by a change in the length of the sample under investigation, and this caused a corresponding change in the frequency of this generator.

The high frequency oscillations generated by both generators were amplified and detected, and the frequency difference obtained, after additional amplification, was fed to an ICh-6 electronic frequency meter. In series with the frequency meter was a vibrator oscillograph and a recording galvanometer or an EPP-09 electronic potentiometer, depending on the rate of the process under investigation. In its most sensitive range, this dilatometer had an amplification of $1 \cdot 10^6$, giving a needle deflection on the frequency meter of 100 mm for a change in sample length of 0.1μ . The samples were used in the form of rods 100 mm long and 2 to 4 mm in diameter.

In Figures 4a and 4b are shown the curves obtained during electroheating of tempered technically pure iron containing 0.02 and 0.07% carbon. In the initial state, the grain of ferrite does not contain a large number of blocks, and the extent of the block boundaries is not large. The transformations along the block boundaries are generated in relatively small spaces, and do not affect the general process of the formation of austenite. Therefore, the breaks in the heating curves and the peaks in the dilatometric curves are observed only at the temperature of polymorphic transformation ($\sim 906^\circ$). In Figures 4c and 4d are presented curves obtained during electroheating of technically pure iron which was first quenched in the stated regime. As a result of an increase in the number of blocks inside the ferrite crystals, which corresponds to an increase in the extent of the block boundaries and the amount of carbon atoms found in these boundaries, the process of the formation of austenite is detected at a temperature of 850° (if the technically pure iron contains 0.02% C) and 830° (if it contains 0.07% C). In addition, the heating curve does not have a temperature break, and a scarcely discernable peak is noted; the dilatometric curve indicates the presence of the process of formation of austenite at the stated temperature.

The peak in the dilatometric curve at 825° was also noted in the work of V.N. Gridnev [18]. The explana-

tion of this experimental result by the presence of a metastable transformation of the martensitic type, which was given in the cited work, seems unsuitable to us. According to our ideas, the observed effect is additional confirmation of the hypothesis of the stable process of the formation of austenite nuclei along the boundaries of the blocks of the mosaic.

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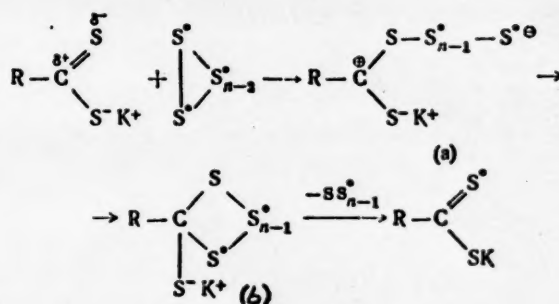
THE MOBILITY OF SULFUR IN THE METHYL ESTER OF DIETHYLDITHIOCARBAMIC ACID AND IN NICKEL ETHYL XANTHATE

I.I. Kukhtenko, L.E. Burkser and G.P. Miklukhin*

(Presented by Academician A.N. Frumkin, July 23, 1955)

According to our previously proposed [1-3] general mechanism of exchange reactions of sulfur in $C=S$ and $C(SX)$ groups, in the first phase, a small chain of elemental sulfur adds to the sulfur in the $C=S$ group of the exchanging compound with the formation of (a).

Exchange, however, becomes possible only when this chain can form a ring with the participation of the central atom giving (b). The greater the negative charge on the atom of sulfur, the faster the exchange proceeds.



Diethoxydithiophosphoric acid $(\text{C}_2\text{H}_5\text{O})_2\text{P}(=\text{S})\text{SH}$, and its salts do not enter into an exchange reaction with

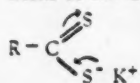
elemental sulfur even at 100° [4], while potassium ethylxanthate reacts rapidly with it even at 0° [2]. We attribute this vast difference in the mobility of the sulfur in the analogously constructed compounds to the inability, in the case of the dithiophosphoric acid, of the type (a) compound to cyclize into (b), since phosphorus, in all cases of similar compounds, does not tend to pass into the pentavalent state [4]. According to the data of A.I. Brodsky and L.V. Sulima [11], phosphoric acid very slowly exchanges its oxygen for the oxygen in water; this was explained on the basis of the difficulty of the phosphorus in this compound to increase its coordination number.

The change in the exchange rate with a change in the negative charge on the sulfur atom in the $C=S$ group was particularly sharp in the derivatives of ethylxanthate and diethyldithiocarbamic acids studied by us. While the sodium salt of the latter exchanged two atoms of sulfur with elemental sulfur at $50-70^\circ$ [3], its methyl ester, as shown in the present work, possesses considerably less mobile sulfur and enters into the exchange re-

*Deceased.

action only at 150-170°. Potassium xanthate exchanges its sulfur at 0°, while nickel xanthate exchanges only at 140°.

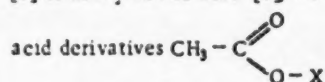
The difference in the mobility of sulfur in salts of the alkali metals, on the one hand, and in esters or salts of heavy metals, on the other hand, can be ascribed to the sharp decrease in the negative charge on the sulfur atom of the C = S group in the latter compounds. Whereas, in sodium or potassium salts conjugation of the type



creates a considerable negative charge on the sulfur atom, in the esters, which contain the covalent S - CH₃ bond, a similar conjugation is considerably less effective and the C = S bond approaches in character the C = S bond of thiones. In accordance with this, exchange in an ester proceeds under approximately the same temperature conditions as the exchange of functional sulfur in 2-mercaptobenzothiazole and other thiones [1,5-7].

The structure of nickel xanthate has not been definitely cleared up. Apparently, this complex compound, like an ester, contains the weakly polar S - Ni bond, and the low mobility of its sulfur must be ascribed to the low negative charge on the sulfur atom of its C = S bond. It is possible that here coordination bonding of the sulfur atom to a second atom of nickel also plays a part.

In investigations of hydrogen-exchange reactions of salts and derivatives of acetic acid with heavy water [8] or heavy acetic acid [9], we observed an analogous influence of the polarity of the O - X bond in the acetic



In conclusion we wish to direct attention to the following. A very few investigations have been made in which salts and complex compounds containing various acid groups were studied. In these works, the influence of the latter groups on the properties of the parent compound were studied. Nevertheless, very little is known of the influence of, for example, sodium, iron, or lead on the acid groups, on the mobility of atoms in them, and on their structure and reactions. At the same time, this influence is enormous, and acetic or xanthic acid residues differ sharply as to the properties of the sodium, nickel, or silver salts. The results of the present and previous work are positive on this score.

We consider that the study of the influence of different metals on the properties of the acid residues bound to them will be carried out on a broader front, and that these investigations will lead not just to isotopic indicator methods only. The discovery that lead acetate condenses with benzaldehyde in the absence of acetic anhydride [10] which is absolutely necessary when the reaction is carried out with sodium acetate, confirms these statements.

EXPERIMENTAL

1. For the investigation of the exchange reaction between an ester and sulfur, toluene solutions of methyl diethyldithiocarbamate and elemental radioactive sulfur were prepared. In each experiment, 2.5 ml of toluene solution containing 0.004 mole of the methyl ester and 13.1 ml of toluene containing 0.004 mole of radioactive sulfur were used. The reacting substances were heated in sealed ampoules at 156, 170, and 175°. Temperature variation did not exceed 0.3°. After opening the ampoule, the solvent was removed under mild vacuum at 30°. In order to remove traces of the ester, the sulfur was washed with a small quantity of ethyl alcohol, recrystallized twice from benzene, and finally washed once more with alcohol on the filter.

The ester was purified by fractionation under high vacuum at 30° (n_D^{25} 1.5812). The original ester, synthesized from diethylamine, carbon disulfide, and methyl iodide, had n_D^{25} 1.5808. The method of separation was checked by a specially conducted experiment in which the solutions of reacting substances, which were mixed at room temperature, were separated immediately in accordance with the above-described method. In this experiment, the sulfur did not decrease in radioactivity, and the ester did not become radioactive (see Table 1). The ester and sulfur resulting from these experiments were oxidized by the method of Carius. The results of the experiments are presented in Table 1. All the activity data are given in number of impulses per minute above background for a weighed sample in 4 mg of benzidine sulfate. The average rate constants, calculated as usual [3], were $K_{av}^{156} = 0.156$ and $K^{170} = 0.915$ hours⁻¹. The half-life of the exchange determined both by the formula $\tau_{1/2} = 0.693/K$ and graphically was 4.5 and 0.75 hours at 156 and 170°, respectively. The activation energy was approximately 40 kcal/mole.

The experimental results establish that the ester exchanges only one sulfur atom with the elemental sulfur,

most probably from the C=S group. The exchange reaction proceeds considerably slower than with the sodium salt of diethyldithiocarbamic acid.

TABLE 1

Exchange Reaction Between the Ester and Sulfur.

Substance	Activity of the original sulfur	Temp., °C	Time, hours	Activity of the substance above background	Sum of the ester and sulfur activities*	Fraction exchanged	K, hr ⁻¹
Ester Sulfur	4355	156	3	$\begin{Bmatrix} 345 \\ 3550 \end{Bmatrix}$	4210	0.32 0.37	0.129 0.154
Ester Sulfur	4355	156	5.5	$\begin{Bmatrix} 595 \\ 3085 \end{Bmatrix}$	4275	0.55 0.68	0.145 0.168
Ester Sulfur	4355	156	8.5	$\begin{Bmatrix} 845 \\ 2710 \end{Bmatrix}$	4400	0.78 0.76	0.178 0.168
Ester Sulfur	4355	170	1	$\begin{Bmatrix} 660 \\ 3040 \end{Bmatrix}$	4360	0.60 0.60	0.915 0.915
Ester Sulfur	4355	170	2	$\begin{Bmatrix} 1050 \\ 2285 \end{Bmatrix}$	4385	0.96 0.94	Equilibrium
Ester Sulfur	4355	170	3	$\begin{Bmatrix} 1155 \\ 2085 \end{Bmatrix}$	4395	1.06 0.96	Ditto
Ester Sulfur	4355	175	4.5	$\begin{Bmatrix} 1130 \\ 2140 \end{Bmatrix}$	4400	1.04 0.98	"
Ester Sulfur	4355	175	9.5	$\begin{Bmatrix} 1130 \\ 2080 \end{Bmatrix}$	4340	1.04 0.96	"
Ester Sulfur	5740	Mixed and separated at 30°	—	$\begin{Bmatrix} 1 \\ 5700 \end{Bmatrix}$	5700	— —	No exchange

*It was considered that one sulfur atom in the ester was exchangeable. Therefore, the true activity of the exchanging sulfur in the ester was twice that measured.

II. For the investigation of the exchange between the sulfur of nickel ethylxanthate (prepared from C_2H_5CSSK and $Ni(NO_3)_2$, recrystallized from benzene) and elemental sulfur, a benzene solution of the latter containing 8 mg of active sulfur per ml and a benzene solution of the ester containing 20 mg of it per ml were prepared. In each experiment, a mixture of equal volumes of both solutions (10 ml) was used. After heating, the benzene solution of sulfur and nickel xanthate was extracted for 3-5 minutes with 7% NH_4OH , and the water and benzene layers were separated. The latter was washed three times with NH_4OH and twice with water, the solvent was evaporated off, and the residual sulfur was recrystallized twice from alcohol.

The water layer, containing nickel ethylxanthate as the ammonium complex, was washed 5 times with benzene and decomposed with acetic acid. The precipitated salt was washed with water, dried, washed with carbon disulfide, and again dried. The thus purified nickel ethylxanthate and also the sulfur after the exchange were oxidized as stated above. The results of the experiments are presented in Table 2. The average rate constants, calculated as before for a first order reaction, were $K^{139} = 0.07$ and $K^{156} = 0.35 \text{ hours}^{-1}$; the half-life of the exchange was 10 and 2 hours at 139 and 150°, respectively.

The results presented in Table 2 show that 4 atoms of sulfur from the nickel salt enter into the exchange reaction. The exchange reaction proceeds significantly slower than in the case of the potassium salt [2].

TABLE 2

Exchange Reaction Between Nickel Ethylxanthate and Sulfur

Substance	Activity of the original sulfur	Temp., °C	Time, hours	Activity of the substance	Sum of the activities of sulfur and salt	Fraction exchanged	K, hr ⁻¹
Salt Sulfur	4650	139	2	$\begin{Bmatrix} 330 \\ - \end{Bmatrix}$	—	0.14 —	0.069 —
Salt Sulfur	4750	139	3.5	$\begin{Bmatrix} - \\ 4190 \end{Bmatrix}$	—	— 0.23	— 0.080
Salt Sulfur	4640	139	8	$\begin{Bmatrix} 930 \\ 3690 \end{Bmatrix}$	4620	0.41 0.40	0.066 0.063
Salt Sulfur	4420	139	9	$\begin{Bmatrix} 1100 \\ 3420 \end{Bmatrix}$	4520	0.51 0.44	0.079 0.064
Salt Sulfur	1300	139	16.5	$\begin{Bmatrix} 515 \\ 680 \end{Bmatrix}$	1195	0.82 0.92	0.110 0.157
Salt Sulfur	1290	139	26	$\begin{Bmatrix} 615 \\ 590 \end{Bmatrix}$	1205	0.98 1.04	Equilibrium Ditto
Salt Sulfur	4530	150	2	$\begin{Bmatrix} 1050 \\ 3440 \end{Bmatrix}$	4490	0.48 0.47	0.325 0.322
Salt Sulfur	18330	150	3.3	$\begin{Bmatrix} 6320 \\ 11900 \end{Bmatrix}$	18220	0.71 0.68	0.373 0.338
Salt Sulfur	4640	150	4	$\begin{Bmatrix} 1830 \\ - \end{Bmatrix}$	—	0.82 —	0.426 —
Salt Sulfur	4610	100	1	$\begin{Bmatrix} 0 \\ - \end{Bmatrix}$	—	No exchange 0	
Salt Sulfur	5030	20	0	$\begin{Bmatrix} 0 \\ - \end{Bmatrix}$	—	No exchange 0	

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ISOMERIC TRANSFORMATION OF XYLENES OVER ALUMINOSILICATES AND THEIR DEMETHYLATION IN THE PRESENCE OF BENZENE

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Academician A.V. Topchiev, G.M. Mamedaliev and G.N. Suleimanov

Symmetrical polyesters presently enjoy exceptionally great importance in the development of synthetic fiber production. Success in the use of polyester fibers has stimulated a broad expansion in investigations directed toward the development of new methods for the production from petroleum fractions of paraxylene, the basic raw material for the production of terephthalic acid which is used in the production of Terylene. One of the most important prospective courses for the development of production of paraxylene is an isomerization process which makes possible the expansion of paraxylene resources by the isomeric transformation of ortho- and metaxylenes.

A.F. Dobryansky and E.F. Saprykin [1] showed that during the pyrolysis of xylenes, along with alkylation, dealkylation, decomposition, and condensation reactions, thermal isomerization of the original xylene also occurs.

The isomerization of xylenes in the presence of aluminum chloride has been studied previously [2-4 and others]. Work on the isomerization of pseudocumene [1,2,4-trimethylbenzene] into mesitylene [1,3,5-trimethylbenzene] [5] and of durene [1,2,4,5-tetramethylbenzene] and isodurene [1,2,3,5-tetramethylbenzene] into prehnitene [1,2,3,4-tetramethylbenzene] [6] is also known. Norris and co-authors [7,8] studied the isomerization of xylenes in the presence of aluminum chloride, promoting the reaction with a stream of hydrogen chloride. The results of the investigations demonstrated the relatively lesser tendency of metaxylene toward isomerization in the presence of aluminum chloride. Ortho- and paraxylene are comparatively easily isomerized. During the period in which the present work was carried out in 1954, a report was published by Bodeker and Emer [9] on the vapor-phase isomerization of technical metaxylene over an aluminosilicate cracking catalyst. With a view to reducing side reactions, cracking, separate experiments were carried out under vacuum. The use of a vacuum, however, contributed to the formation of appreciable amounts of ethylbenzene.

During a study of the demethylation of orthoxylene and the conjugate methylation of benzene, we showed that in the treatment of these hydrocarbons over a synthetic aluminosilicate, isomerization of orthoxylene also occurred along with the stated reactions. This conclusion, arrived at on the basis of experimental work carried out by us in 1953-1954, served as the basis for carrying out special investigations on the isomerization of the individual isomeric xylenes.

In the present communication are presented fundamental data from the investigations on the isomerization of xylenes and their demethylation in the presence of benzene over synthetic aluminosilicates*.

The experiments on the catalytic treatment of a mixture of orthoxylene and benzene were carried out in a laboratory flow-type apparatus. Samples of granular, synthetic aluminosilicate were used as the catalyst. The benzene used in this work was chemically pure for cryoscopy, and had the following properties: initial boiling point 79.74°, final boiling point 80.10°, bromine number 0.03, sp. gr. 0.8782, 99.6% sulfonatable, n_D^{20} 1.5010. The orthoxylene boiled in the range 143-144°, sp. gr. 0.8798, n_D^{20} 1.5050, 100% sulfonatable. Analysis by the Ullman oxidation method gave 98.7% ortho- and 1.3% meta-isomer.

*The results of part of these investigations were presented to the Scientific Council of the State Institute for the Nitrogen Industry USSR in July 1955. Further work in this direction was continued by us in cooperation with the Nitrogen Institute.

TABLE 1

Isomeric transformation of Xylenes over Aluminosilicates.

Process characteristics and product properties	Temp. 450°, pressure 1 atm., rate 0.5:1, cycle length 50 min		Temp. 450°, pressure 50 mm Hg, rate 0.5:1, cycle length 50 min	
	Orthoxylene feed	Isomernate	Metaxylene feed	Isomernate
Material, weight %				
Catalyzate	—	97.60	—	97.20
Coke	—	0.90	—	0.59
Gas	—	0.12	—	0.28
Loss	—	1.38	—	1.93
Fractional composition of the product				
Initial b.p., °C	139.5	105	130	134
To 108°C, %	—	0.5	—	—
108-113°	—	1.8	—	—
113-118°	—	1.76	—	—
118-125°	—	1.40	—	—
125-132°	—	1.76	0.45	—
132-136°	—	1.70	1.25	1.89
136-140°	1.33	69.16	95.26	92.87
140-146°	91.73	9.9	—	—
146-150°	—	1.80	—	—
150-160°	—	3.06	—	—
End point 160°	—	2.70	—	—
End point, °C	144	163	140	138
Overall yield, %	94.77	95.54	96.96	94.76
Residue, %	3.75	3.05	2.18	4.0
Loss, %	1.48	1.41	0.86	1.24
Sp.gr.	0.8818	0.8715	0.8634	0.8642
n_D^{20}	1.5055	1.5003	1.4970	1.4980
Chemical composition of the product, wt. %				
o-xylene	98.7	—	—	27.8
m-xylene	1.3	—	98.0	50.4
p-xylene	—	—	2.0	21.8
Properties of 136-140° fraction				
Yield based on catalyzate, %	1.33	69.16	—	—
d_4^{20}	0.8816	0.8696	—	—
n_D^{20}	1.5052	1.4994	—	—
Chemical composition of the fraction [136-140°] wt. %				
o-xylene	—	30.3	—	—
m-xylene	—	51.6	—	—
p-xylene	—	23.1	—	—
Properties of the 140-146° fraction				
Yield based on catalyzate, %	91.7	9.9	—	—
d_4^{20}	0.8816	0.8735	—	—
n_D^{20}	1.5051	1.5022	—	—

A study was carried out on the influence of pressure, temperature, rate, and cycle length on the reaction, and the optimum values of the parameters for xylene production were established. At a temperature of 525°, a pres-

sure of 15 atm., a rate of 0.5:1, and a cycle length of 50 minutes, a single pass of the mixture of orthoxylene and benzene, 1:2 mole ratio, lead to the production of 94-95% catalyzate, 1.9-2.2% coke, and 1.7-2.3% gas. The process is chiefly characterized by the occurrence of the conjugate reactions of alkylation and dealkylation which leads to the formation of up to 27-28% toluene in the catalyzate. The isomeric transformation of ortho-xylene with the formation of the meta- and para-isomers was also observed. As a consequence of this, there was a corresponding lowering of specific gravity, refractive index, and boiling range of the product. Spectral analysis of the xylene fraction of the catalyzate indicated the presence of 16% ortho-, 38% meta-, and 23% para-xylene and 20% ethylbenzene. Analogous investigations were carried out on the catalytic demethylation of metaxylene and the conjugate methylation of benzene. The data obtained did not differ from those obtained during the experiments with orthoxylene.

The chief results of the investigation of the isomeric transformation of ortho- and metaxylene are presented in Table 1.

The influence of various factors was studied, and optimum values of the conditions for the isomerization process were established. It was shown that the use of pressure directed the process toward disproportionation of the xylene with the formation of appreciable amounts of toluene and trimethylbenzene. For the isomerization of orthoxylene, satisfactory results were obtained at atmospheric pressure and a temperature of 450°. The yield of catalyzate under these conditions was 97.5%, gas was 0.12%, and coke was 0.8-0.9%. Analysis of the xylene fraction of the catalyzate obtained under optimum conditions indicated 22-24% paraxylene, 43-48% metaxylene, and 29-30% orthoxylene.

The use of a vacuum considerably reduced the disproportionation of xylene. Isomerization of metaxylene was carried out in a flow-type apparatus working under vacuum. The experiments were carried out at a temperature of 450°, a rate of 0.5:1, a cycle length of 50 minutes, and a pressure of 50 mm Hg. The chief results of a characteristic experiment on the isomerization of metaxylene are presented in Table 1. As seen from these data, metaxylene was isomerized without any side reactions. There was no marked change in the boiling range of the products. Formation of gas was not observed. The amount of coke deposited on the catalyst did not exceed 0.6-0.8%. The yield of isomerizate was 97.2%. Spectral analysis of the isomerizate indicated that it contained 27.8% ortho-, 50.4% meta, and 21.8% paraxylene.

The presence of a small amount of xylenes, apparently formed by isomerization of the original alkylaromatic hydrocarbons, was established in the products of the catalytic treatment of ethylbenzene and isopropylbenzene over aluminosilicates. Upon oxidation of the catalyzate with an alkaline solution of potassium permanganate, according to Ullman, along with benzoic acid certain amounts of phthalic acids were obtained.

These observations require further study. Work on the isomeric transformation of different aromatic hydrocarbons in the indicated direction is being continued.

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